

## Thermal effect in unoccupied molecular orbitals of C<sub>60</sub> molecules adsorbed on a Si(001)-(2 × 1) surface studied by NEXAFS

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We report here the temperature-dependent unoccupied molecular orbitals (MO's) of C<sub>60</sub> molecules adsorbed on a Si(001)-(2 × 1) surface measured using near edge x-ray absorption fine structure (NEXAFS). At 300 K, the NEXAFS spectrum reveals that the interaction between a 1.0 monolayer (ML) C<sub>60</sub> film and a Si(001) surface is mainly the van der Waals force. After annealing the samples at 500 K, we observe an increment in the full-width at half-maximum of unoccupied MO's, which indicates the change of the interaction. Moreover, the lowest unoccupied molecular orbital (LUMO) shifts to the higher photon energy side and the intensity of the LUMO+1 relative to that of the LUMO+3 decreases in the NEXAFS spectrum. These results suggest that the strong interaction induced at 500 K has a covalent character, to which the LUMO+1 contributes.

**Keywords:** Si(001) surface; Fullerenes; NEXAFS.

### 1. Introduction

The interaction of fullerenes with semiconductor and metal surfaces is important to understand their physical and chemical properties and to develop their new material functions. The recent observation of epitaxial silicon carbide (SiC) formations by the thermal reaction of C<sub>60</sub> molecules with a Si surface (Hamza *et al.*, 1994) has increased an interest in the interaction between C<sub>60</sub> molecules and the Si surface. Extensive experimental studies have been performed on a Si(001)-(2 × 1) surface, using scanning tunneling microscopy (STM), high-resolution electron-energy-loss-spectroscopy (HREELS) and photoelectron spectroscopy (PES).

Using STM, C<sub>60</sub> molecules are observed to adsorb selectively between the dimer-rows at a coverage lower than 1.0 monolayer (ML), and grow with the layer-plus-island growth mode above 1.0 ML at 300 K (Wang *et al.*, 1993; Chen & Sarid, 1995). The coverage of the 1.0 ML corresponds to the adsorption of two molecules in the 4 × 3 super lattice on the Si(001) surface (Wang *et al.*, 1993; Klyachko & Chen, 1995). HREELS (Suto *et al.*, 1997) and PES (Sakamoto *et al.*, 1999) measurements show that the interaction between the 1.0 ML C<sub>60</sub> film and the Si(001)-(2 × 1) surface is mainly the van der Waals force. After annealing the 1.0 ML C<sub>60</sub> film at 500 K, a strong interaction is reported to be induced using

HREELS (Sakamoto *et al.*, 1998) and PES (Kondo *et al.*, 1999). The HREELS study reports that the interaction has an ionic character from the measurement of the vibrational excitations of a C<sub>60</sub> molecule, in which the following assumption is used. That is, the energies of the vibrational excitations of a C<sub>60</sub> molecule shift linearly with the amount of the charge transferred to the lowest unoccupied molecular orbital (LUMO) of a C<sub>60</sub> molecule (Rice & Choi, 1992). On the other hand, PES indicates that the interaction has a strong covalent character from the observation of the bonding orbital between C<sub>60</sub> molecules and the Si(001) surface. This contradiction whether the interaction at 500 K is ionic or covalent, is not resolved until now.

On metal surfaces, the character of the interaction is discussed whether a partial occupied LUMO is observed or not in the PES spectra (Chase *et al.*, 1992; Tsuei *et al.*, 1997; Maxwell *et al.*, 1998). On Si surfaces, though the behavior of the charge transfer is observed using PES, no peak derived from the LUMO has been observed yet because of the small cross section of the partial occupied LUMO and/or the small amount of the charge transferred from the Si(001) surface. The near edge x-ray absorption fine structure (NEXAFS) is a suitable technique to elucidate the behavior and contribution of the LUMO to the interaction with the Si(001) surface and solve the contradiction due to the direct observation of the unoccupied molecular orbitals of a C<sub>60</sub> molecule. In this paper, we present the temperature-dependent NEXAFS spectra of C<sub>60</sub> molecules adsorbed on the Si(001)-(2 × 1) surface.

### 2. Experiment

NEXAFS measurement was carried out in a ultrahigh-vacuum (UHV) system at the soft x-ray beam line BL-7A of the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The UHV system consists of an analysis chamber and a sample preparation one. The analysis chamber is equipped with a low energy electron diffraction (LEED) system and a quadropole mass spectrometer. The preparation chamber was used for the deposition of C<sub>60</sub> molecules. The pressures were below 1 × 10<sup>-10</sup> Torr in the analyzer chamber and below 1 × 10<sup>-9</sup> Torr in the preparation one. We obtained the polarization-dependent C-K edge NEXAFS spectra by partial electron yield detection with a retarding voltage of 100 V. The x-ray incident angles were 0°, 35° and 75° for the measurement of the polarization-dependence relative to the surface normal direction. The energy resolution of the NEXAFS measurement was 0.5 eV. All measurements were performed at 300 K.

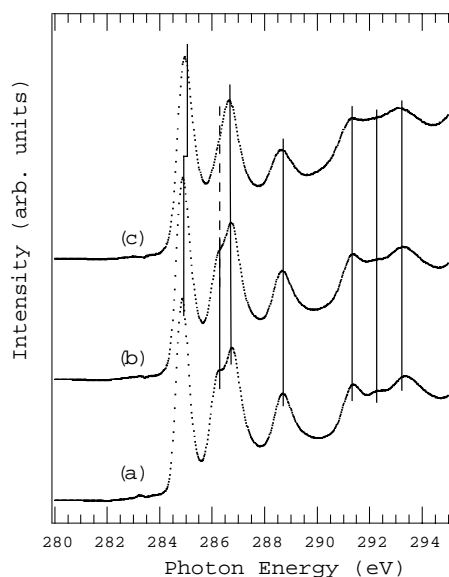
The *p*-type Si(001) substrate (1000 Ω-cm) was first prepared chemically following the Shiraki method (Ishizuka & Shiraki, 1986) and then introduced into the UHV chamber. The sample was outgassed at 1150 K for 10 minutes and annealed at 1520 K for 5 seconds by resistive heating, to get a clean reconstructed Si(001)-(2 × 1) surface. The cleanliness of the sample was checked by the observation of a sharp 2 × 1 pattern using LEED. We spontaneously cooled down the samples to 300 K for several minutes, before the deposition of C<sub>60</sub> molecules. The method about the C<sub>60</sub> purification and deposition is described elsewhere (Sakamoto *et al.*, 1999).

### 3. Results and discussion

Figure 1 shows the C-K edge NEXAFS spectra measured at 300 K. (a) and (b) are the NEXAFS spectra of the 5.0 and 1.0 ML C<sub>60</sub> films adsorbed on a clean Si(001)-(2 × 1) surface, respectively. The spectrum in (c) is obtained after annealing the 1.0 ML C<sub>60</sub> film

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adsorbed Si(001) surface at 500 K. The x-ray incident angle was  $0^\circ$  for all spectra in Fig. 1, because no polarization-dependence is observed due to the high symmetry of a  $C_{60}$  molecule. All spectra are normalized by the intensity at 290 eV after subtracted the background and then divided by the clean Si(001) surface spectrum. In Figs. 1(a) and (b), we observe the resonance peaks from the C 1s core level to the unoccupied molecular orbitals (MO's) of a  $C_{60}$  molecule at photon energies of 284.9, 286.3, 286.8, 288.7, 291.3, 292.3 and 293.2 eV. Taking into account the photon energies of the unoccupied MO's reported previously, (Tsuei *et al.*, 1997, Maxwell *et al.*, 1998), the 284.9-, 286.3-, 286.8- and 288.7-eV peaks are assigned to be the lowest unoccupied molecular orbital (LUMO), the second one (LUMO+1), the third one (LUMO+2) and the fourth one (LUMO+3), respectively. The LUMO and LUMO+1 are threefold degenerate MO's that have  $t_{1u}$  and  $t_{1g}$  symmetries in the  $I_h$  point group, respectively. The NEXAFS spectrum in (b) has the same peak positions and the same energy profile as that in (a). Since a 5.0 ML film is considered to be a bulk  $C_{60}$ , this result indicates that the 1.0 ML  $C_{60}$  film interacts weakly with the Si(001) surface.

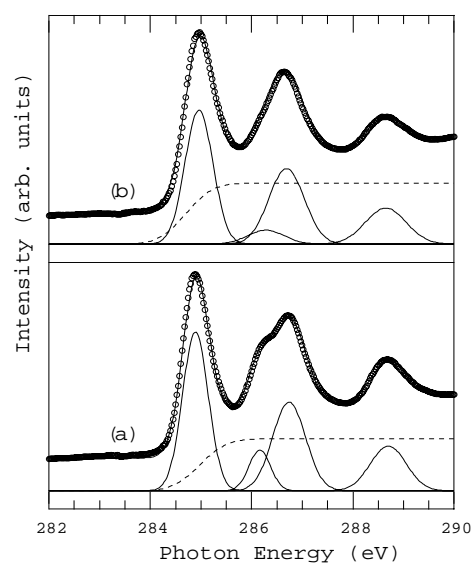


**Figure 1**

Temperature-dependent NEXAFS spectra. (a) and (b) are the NEXAFS spectra of the 5.0 and 1.0 ML  $C_{60}$  film adsorbed on a Si(001)-(2 $\times$ 1) surface at 300 K. (c) is obtained after annealing the 1.0 ML film at 500 K.

After annealing the 1.0 ML  $C_{60}$  film adsorbed on the Si(001) surface, three changes are observed in the spectrum. First, a broadening in full-width at half-maximum (FWHM) of the unoccupied MO's. Second, an apparent disappearance of the LUMO+1. And third, a 0.1-eV shift of the LUMO to the higher photon energy side. The broadening in FWHM suggests the removal of the degeneracy of MO's, and therefore that a strong interaction between the 1.0 ML  $C_{60}$  film and the Si(001) surface is induced at 500 K. To clarify the second and third changes, we deconvolute the NEXAFS spectra using a least-square fitting method with a Gaussian line shape. The result of the deconvolution indicated in Fig. 2. (a) is the NEXAFS spectrum of the 1.0 ML  $C_{60}$  film adsorbed Si(001) surface and that in (b) is the spectrum obtained after annealing the 1.0 ML  $C_{60}$  film at 500 K. The circles and solid lines are the experimental

data and the results of the fitting, respectively. The components decomposed in the fitting procedure are also indicated in Fig. 2. In Table 1, we show the parameters used in the fitting procedure. From the fitting results, we know that the LUMO+1 remains at 500 K. Regarding the FWHM, the FWHM of the LUMO+1 becomes much broader than those of other unoccupied MO's. The FWHM of the LUMO+1 changes from 0.50 to 0.85 eV and that of the LUMO from 0.60 to 0.65 eV. Moreover, the LUMO+1 seems to become smaller and shifts 0.1 eV to the higher photon energy side.



**Figure 2**

The results of the deconvolution of the NEXAFS spectra in Fig. 1. Details are explained in the text.

In order to obtain the intensity ratio of the LUMO, LUMO+1 and LUMO+2, we compare their intensities with that of the LUMO+3 which is considered to have no change by the thermal process. The intensity ratios of  $I_{LUMO}/I_{LUMO+3}$ ,  $I_{LUMO+1}/I_{LUMO+3}$  and  $I_{LUMO+2}/I_{LUMO+3}$  are 2.52, 0.54 and 1.81 for the 1.0 ML  $C_{60}$  film at 300 K and 2.54, 0.34 and 1.80 for that at 500 K.  $I_{LUMO}$ ,  $I_{LUMO+1}$ ,  $I_{LUMO+2}$  and  $I_{LUMO+3}$  are the integrated intensity of the LUMO, LUMO+1, LUMO+2 and LUMO+3, respectively. It is found that the intensity of the LUMO does not change and that of the LUMO+1 decreases by annealing at 500 K. This result suggests that the LUMO+1 contributes to the strong interaction and the LUMO has little contribution to it.

On a Cu(111) surface where the interaction of the 1.0 ML  $C_{60}$  film with the substrate is ionic, the intensity of the LUMO is reported to decrease due to the charge transfer from the substrate to the LUMO of a  $C_{60}$  molecule (Tsuei *et al.*, 1997). In addition, the LUMO shifts to the lower photon energy side on the Cu(111) surface. On Al(111) and Al(110) surfaces where the 1.0 ML  $C_{60}$  film interacts covalently with the substrate, the NEXAFS spectra show that the LUMO shifts 0.45 eV to the higher photon energy side with no change in intensity, and the intensity of the LUMO+1 decreases (Maxwell *et al.*, 1998). In the comparison with these metal surfaces, the behavior of the NEXAFS spectra in Figs. 1 and 2 suggests that the interaction at 500 K has not an ionic character but a covalent one, to which the LUMO+1 contributes. Taking into account the change in relative intensity of the LUMO+1 from 0.54 to 0.34 and the threefold degeneracy of the LUMO+1, we consider

that  $6-6 \times 0.54/0.34 \approx 2$  electrons contribute to the hybridization. Here, we have used the assumption that the cross section of the LUMO+1 is the same at 300 and 500 K. Thus, due to the strong interaction, the degeneracy of the LUMO+1 is removed and one unoccupied MO derived from the LUMO+1 hybridizes with the dangling bonds of a Si(001) surface. This hybridization leads to the decrease in intensity and the 0.1-eV shift of the LUMO+1 observed in the NEXAFS spectra. Therefore, we conclude that the interaction between the 1.0 ML C<sub>60</sub> film and the Si(001) surface induced at 500 K, has a covalent character, to which the LUMO+1 contributes due to the hybridization with the dangling bonds of the Si(001) surface. Since the LUMO+1 is reported to be the most disperse of the occupied and unoccupied MO's of a C<sub>60</sub> molecule, and to contribute to the intermolecular interaction (Jost *et al.*, 1991), it is reasonable to consider that the LUMO+1 plays an important role in the interaction with the Si(001) surface.

**Table 1**

The photon energies, Gaussian width and intensities of the decomposed component for NEXAFS spectra.

		Photon Energy (eV)	Gaussian Width (eV)	Relative Intensity
300 K	LUMO	284.9	0.60	1.05
	LUMO+1	286.2	0.50	0.27
	LUMO+2	286.7	0.77	0.59
	LUMO+3	288.7	0.83	0.30
500 K	LUMO	285.0	0.65	0.78
	LUMO+1	286.3	0.85	0.08
	LUMO+2	286.7	0.82	0.42
	LUMO+3	288.7	0.95	0.21

Finally, we mention briefly about the contradiction between HREELS and PES observed at 500 K. The charge transfer scheme applied in HREELS assumes that the symmetry of a C<sub>60</sub> molecule does not change. It is not appropriate in the case of the Si(001) surface, because the change in the symmetry is clearly observed in the NEXAFS spectra. In addition, the LUMO has little contribution to the interaction and then a simple charge transfer scheme seems to be not suitable. The behavior of the ionic interaction observed in PES (Kondo *et al.*, 1999) is considered to be explained not by simple charge transfer but the hybridization of the LUMO+1 with the dangling bonds of the Si(001) surface.

#### 4. Conclusion

We have studied the temperature-dependent NEXAFS spectra of the 1.0 ML C<sub>60</sub> film adsorbed on a Si(001)-(2×1) surface. The NEXAFS spectrum of the 1.0 ML C<sub>60</sub> film has the same peak positions and the same profile with that of the 5.0 ML C<sub>60</sub> film at 300 K. These results show that the interaction between the 1.0 ML C<sub>60</sub> film and the Si(001) surface is mainly the van der Waals force. After annealing the 1.0 ML C<sub>60</sub> film at 500 K, the FWHM's of the unoccupied MO's increase. The larger FWHM indicates that the strong interaction between the C<sub>60</sub> film and the Si(001) surface is induced at 500 K. By the deconvolution of the NEXAFS spectra, we know that the strong interaction at 500 K is originated from the hybridization between the LUMO+1 and the dangling bonds of the Si(001) surface. This suggests that the interaction induced at 500 K has not an ionic character but a covalent character in comparison with the cases of the metal surfaces.

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#### References

- Chase, S. J., Bacsa, W. S., Mitch, M. G., Pilione, L. J. & Lannin, J. S. (1992). *Phys. Rev. B* **46**, 7873–7877.
- Chen, D. & Sarid, D. (1994). *Surf. Sci.* **318**, 74–82.
- Hamza, A. V., Balooch, M. & Moalem, M. (1994). *Surf. Sci.* **317**, L1129–L1135.
- Ishizaka, A. & Shiraki, Y. (1986). *J. Electrochem. Soc.* **33**, 666–671.
- Jost, M. B., Troullier, N., Poirier, D. M., Martins, J. L., Weaver, J. H., Chibante, L. P. F. & Smalley, R. E. (1991). *Phys. Rev. B* **44**, 1966–1969.
- Klyachko, D. & Chen, D. M. (1995). *Phys. Rev. Lett.* **75**, 3693–3696.
- Kondo, D., Sakamoto, K., Ushimi, Y., Harada, M., Kimura, A., Kakizaki, A. & Suto, S. (1999). *Jpn. J. Appl. Phys. Suppl.* **38-1**, 328–331.
- Maxwell, A. J., Brühwiler, P. A., Arvanitis, D., Hasselström, J., Johansson, M. K. -J., & Mårtensson, N. (1998). *Phys. Rev. B* **57**, 7312–7326.
- Rice, M. J. & Choi, H. -Y. (1992). *Phys. Rev. B* **45**, 10173–10176.
- Sakamoto, K., Harada, M., Ashima, H., Suzuki, T., Wakita, T., Kasuya, A. & Suto, S. (1998). *J. Electron Spectrosc. and Relat. Phenom.* **88-91**, 897–903.
- Sakamoto, K., Kondo, D., Ushimi, Y., Harada, M., Kimura, A., Kakizaki, A. & Suto, S. (1999). *Phys. Rev. B* **60**, 2579–2591.
- Suto, S., Sakamoto, K., Wakita, T., Hu, C. -W. & Kasuya, A. (1997). *Phys. Rev. B* **56**, 7439–7445.
- Tsuei, K. -D., Yuh, J. -Y., Tzeng, C. -T., Chu, R. -Y., Chung, S. -C. & Tsang, K. -L. (1997). *Phys. Rev. B* **56**, 15412–15420.
- Wang, X. -D., Hashizume, T., Shinohara, H., Saito, Y., Nishina, Y. & Sakurai, T. (1993). *Phys. Rev. B* **47**, 15923–15930.