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Electronic structure of octane on Cu(111) and Ni(111) studied by near edge X-ray absorption fine structure

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The electronic structure of an octane film grown on Cu(111) and Ni(111) was studied using C K-edge near edge X-ray absorption fine structure (NEXAFS). A pre-peak was observed on the bulk edge onset for the 1 ML thick octane films on the metal substrates. The pre-peak originated from metal-induced gap states (MIGS) in the band gap of octane. The intensity of the pre-peak for octane/Ni(111) was the same as that of octane/Cu(111), suggesting that there was little difference in the density of unoccupied MIGS between the octane film on Ni(111) and Cu(111). We discuss the metal dependence of the density of unoccupied MIGS on the band structure of the metals.

Keywords: Near edge extended X-ray absorption fine structure, Surface electronic phenomena, Alkanes, Copper, Nickel

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1: Introduction

The interaction between alkanes and metals has attracted wide attention [1-5]. This is due to the fact that many catalytic processes involve the conversion of saturated hydrocarbons to various products, and also because n-alkane is the simplest molecule among the saturated hydrocarbons. The adsorption energies of n-alkane molecules on metal substrates are rather small (of the order of 10 kJ/mol/CH₂ chain) [2], and the n-alkane-metal interaction has been categorized to be typical of physical adsorption. However, a softening of the C-H vibration has been observed for the n-alkane/metal system with vibrational spectroscopy [3,4]. The softening indicates that the simple physical adsorption picture is too simplified and there should be some interaction between n-alkanes and metals. Thus, it is attractive to know the electronic structure at the n-alkane/metal interface.

Despite the interest in the electronic structure at the n-alkane/metal interface, it is rather difficult to study the electronic structure at the interface, especially the formation of new in-gap states. The signal from the interface is obscured by the signal from the substrate with the conventional methods, such as ultra violet photoemission spectroscopy, X-ray photoemission spectroscopy [6]. Here, we pay attention to the near edge X-ray absorption spectra (NEXAFS). NEXAFS is based on the X-ray absorption by atoms, and thus, it is atomic species selective. We can study the electronic structure of the molecule itself with negligible influence from the substrate [7,8]. In the present study, we have investigated the atomic and electronic structure of the octane films grown on metals substrates with NEXAFS.

With regard to the NEXAFS study of the octane films on metal substrates, Ostrom et al. have studied an octane film on Cu(110) [5]. They observed a pre-peak just below the bulk edge onset in the C *K*-edge NEXAFS. The pre-peak was ascribed to be metal induced gap states (MIGS). We have also showed the existence of MIGS at the tetratetracontane (C₄₄H₉₀)/Cu(111) interface. While the formation of MIGS for octane on Cu and Au substrates has been experimentally and theoretically clarified, the MIGS on **less noble transition metals**,

such as Fe, Co, Ni, has not been studied satisfactorily, although there are some theoretical studies for these metals. In the case of Cu, the 4s band is close to the Fermi level, while the Ni 3d band is close to the Fermi level. It is interesting to investigate the effect of the metal 3d band on the formation of MIGS. To our knowledge, there is no experimental study to compare the MIGS between on Cu and Ni substrates. In the present study, we have studied the atomic and electronic structures of octane films on Ni (111) and Cu(111).

2: Experimental:

The experiments were performed with an ultra high vacuum (UHV) chamber at the soft X-ray beam line (BL-7A) of the Photon Factory in High Energy Accelerator Research Organization. Mechanically and electrochemically polished Ni and Cu(111) crystals were cleaned by repeated cycles of Ar⁺ sputtering and annealing at 900 K. The sample temperature was monitored with a chromel-alumel thermocouple, which was spot-welded on a Ta sheet attached to the sample surface. The surface cleanliness was checked by C K-edge NEXAFS spectra and C 1s XPS. The octane was purified by repeated freeze-pump-thaw cycles. The octane films were prepared by exposing Ni, Cu(111) substrates to gaseous octane with a gas doser. The substrate temperature was kept at 180 K and 120 K for the octane 1 mono layer (ML) and 50 ML thick films, respectively. **Since the position of NEXAFS and XPS peaks did not shift with further increases in film thickness, the 50 L thick film can be regarded as a bulk sample. In the following, the 50 ML thick film was referred to as a multi layer film. The photon energies were calibrated by the lowest-energy 1s- π^* peak of graphite (285.5 eV).** C K-edge NEXAFS spectra were obtained by the partial electron yield method using a micro-channel plate (MCP) with a retarding voltage of -200 V. C 1s XPS were taken at the normal emission using a hemispherical electron energy analyzer (GAMMADATA SCIENTA, SES-2002).

3: Results and Discussion

Figure 1 shows the polarization dependence of the NEXAFS spectra of the 1 ML thick octane films grown on Cu(111) and Ni(111), together with those of the multi layer octane film. **All the spectra were obtained by pre-edge background subtraction and normalization by their edge-jump.** In the spectra of the multi layer octane film, sharp C1s-to- σ^* (C-H) and broad C1s-to- σ^* (C-C) peaks are observed at 288 eV and 293 eV. The σ^* (C-C) peak is assigned to the transition whose transition moment is parallel to the molecule's long axis [9]. We first discuss the structure of the octane film by discussing the polarization dependence of these two peaks. The intensity of the σ^* (C-C) peak was larger for normal X-ray incidence (90°), while the σ^* (C-H) peak was larger for grazing X-ray incidence. The polarization dependence can be analyzed in terms of the transition momentum as

$$\mu = \int \phi_f^* E \cdot P \phi_i d\tau \quad (1),$$

where E is the electric vector of the X-ray, P is the momentum operator of the excited electron, and ϕ_i and ϕ_f are the initial- and final-state wave functions [10]. Here, ϕ_i is the wave function of the 1s orbital and ϕ_f is the π^* or σ^* molecular orbital. Equation (1) indicates that the value of μ is greatest for E along the molecular orbital, while μ becomes zero for E perpendicular to the orbital. **Since the σ^* molecular orbital is parallel to the molecular long axis, the $1s \rightarrow \sigma^*$ (C-C) transitions occur for E parallel to the molecular long axis.** The molecular orientation angle was quantitatively evaluated by fitting the intensity of the peaks to the theoretical curves obtained by equation (1). Using the polarization dependence of the σ^* (C-C) peak, the mean inclination angle of the octane molecules from the surface was determined to be $15(\pm 10)^\circ$ on both substrates (lying-down configuration). The lying-down configuration agreed with our previous results of the n-C₄₄H₉₀ (TTC) film on Cu(001) [8].

We then discuss the energy of the σ^* (C-H) and σ^* (C-C) peaks to investigate the interaction between the octane film and metal substrates. While the peak energy of the σ^* (C-H) for the 1 ML thick octane film on metals did not change from that of the multi layer

octane film, the $\sigma^*(\text{C-H})$ peak observed at 288.2 eV for the multi layer film split into two 287.2 eV and 289.4 eV peaks for the 1 ML thick octane films on metals. The peak splitting might come from the interaction of the octane film with the substrate. In the lying-down configuration, one-half of the hydrogen atoms touched the substrate, while the other half faced the vacuum, and in this case the (C-H) state should be split in two - a strongly interacting state and a less interacting one.

The electronic structure of the octane film on metal substrates was also investigated by XPS. Figure 2 shows the C 1s XPS of the 1 ML thick octane films on Cu(111) and Ni(111), and the multi layer octane film. **The binding energy was given with respect to the Fermi level.** Even for the multi layer films, the position of C1s XPS peak did not change with time, indicating that the charged up effect can be neglected in the present system. The binding energy of C 1s was 286.4 eV for the multi layer octane film. It decreased by ~ 0.7 eV for the 1 ML thick octane film on Cu(111) and it decreased by 1.0 eV on Ni(111). **The decrease in the binding energy of C 1s for the 1 ML thick film can be explained by the initial state and final state effect. In terms of the initial state effect, the decrease in the binding energy indicated that an electron was transferred from the metal substrate to the octane film. In terms of the final state effect, the decrease in the binding energy indicated the larger screening of the core-hole. On a metal surface, the core-hole can be effectively screened by the substrate electron. With these results, we cannot decide which effect is dominant.**

We then pay attention to the metal induced gap states at the interface. Figure 3 shows the pre-edge feature of the 1 ML thick octane film on Ni (111) and Cu(111). A pronounced pre-peak appeared just below the bulk edge onset for the 1 ML thick octane film. Since NEXAFS qualitatively provides information on the density of unoccupied states, the appearance of the pre-peak below the edge indicates that new states were formed below the vacuum level and above the Fermi level. The adsorption energies of octane molecules on metal surfaces are rather small (of the order of 10 kJ/mol/ CH_2 chain), and the

molecule-surface interaction is not chemisorption, but is typical of physisorption. Therefore, the pre-peak observed by NEXAFS originated not from a strong chemical bond at the interface, but from the states formed by the proximity to a metal. The states could be qualitatively understood as metal induced gap states, MIGS [7,8]. The formation of MIGS at alkane/metal interfaces agreed with the previous study of octane/Cu(110) [5] and TTC/Cu(001) [8].

The character of the MISG is discussed in more detail. The signal of the MIGS component was obtained by subtracting the bulk component from the spectra (See Fig. 3). **In the higher photon energy regime, the signal of the MIGS component was negative. This can be explained by the difference in the conduction band of the octane film. The density of states at the bottom part of the conduction band might be smaller for the 1 ML film than multi layer films. Here, it should be noticed that the position of MIGS band was far apart from the conduction band. Therefore, the position and intensity of the peak were not affected by the background subtraction, and we can discuss the intensity of MIGS using the signal of the MIGS component in Fig. 3.** The intensity of the MIGS was larger for the grazing X-ray incidence than normal X-ray incidence on both Ni(111) and Cu(111), indicating that the MIGS had a p_z like structure. This character of MIGS agreed with other insulator/metal systems, such as alkali halides/metals and organic insulator crystals/metals [7,8]. Then, we compared the intensity of the pre-peak observed for the 1 ML thick octane films on Cu(111) and Ni(111). The intensity of the pre-peak was 0.27 and 0.30 (in arbitrary units) for octane/Ni(111) and octane/Cu(111). The intensity of the pre-peak for octane/Ni(111) was the same as that for octane/Cu(111), while the XPS results suggested that interaction between the octane films and the metal substrate was larger for octane/Ni(111) than octane/Cu(111). We discuss the reason why there was little difference in the intensity of the pre-peak between Ni(111) and Cu(111). Figure 4 shows the schematic energy diagram for MIGS in octane/Cu(111) and Ni(111) obtained by first-principles (density functional theory)

electronic-structure calculations [8]. The MIGS band of octane/Ni lies below the Fermi level, so the density of states in the unoccupied side is small, while the density of occupied states is large. By contrast, the Fermi level runs right through the MIGS band when the substrate is Cu, but the density of MIGS is relatively low due to a low density of states of the Cu 4s band. As a consequence, there was little difference in the states between octane/Ni and octane/Cu as far as the density of *unoccupied* MIGS is concerned. This band picture is consistent with the results obtained by NEXAFS, which measures the MIGS in the unoccupied side. While the density of MIGS in the unoccupied side was the same in both Cu(111) and Ni(111), the density of MIGS in the occupied side for octane/Ni(111) is predicted to be much larger than that for octane/Cu(111). The difference could be detected by an experimental method that detects occupied states, such as resonant photoemission or X-ray emission spectroscopy.

4 Conclusion

Atomic and electronic structures of the octane films on Cu(111) and Ni(111) were studied with NEXAFS. The molecule was adsorbed on both substrates with its molecular long axis parallel to the surface. For the 1 ML film, we have obtained clear evidence that MIGS were formed at the octane/metal interfaces. The density of unoccupied MIGS states at octane/Ni was close to that at octane/Cu. The small difference in the states can be explained by the band structures of Ni and Cu.

Acknowledgments

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Figures captions

Fig. 1: C-K edge NEXAFS spectra of the 1 ML thick octane films grown on Cu(111) and Ni(111) for X-ray incident angles varied over 30°, 55°, 90°. The result of a multilayer octane film on Cu(111) was shown for comparison. All the spectra are normalized by their edge-jump.

Fig. 2: C-1s XPS spectra of the 1 ML thick octane films grown on Cu(111) and Ni(111), and the multilayer octane film on Cu(111).

Fig. 3: Blowup of the pre-peaks in the NEXAFS of the 1 ML thick octane films grown on Cu(111) and Ni(111) obtained by subtracting the bulk (multilayer) spectrum, which has no structure at the edge onset.

Fig. 4: A schematic energy diagram for MIGS of the 1 ML thick octane films grown on Cu(111) and Ni(111).

Fig. 1

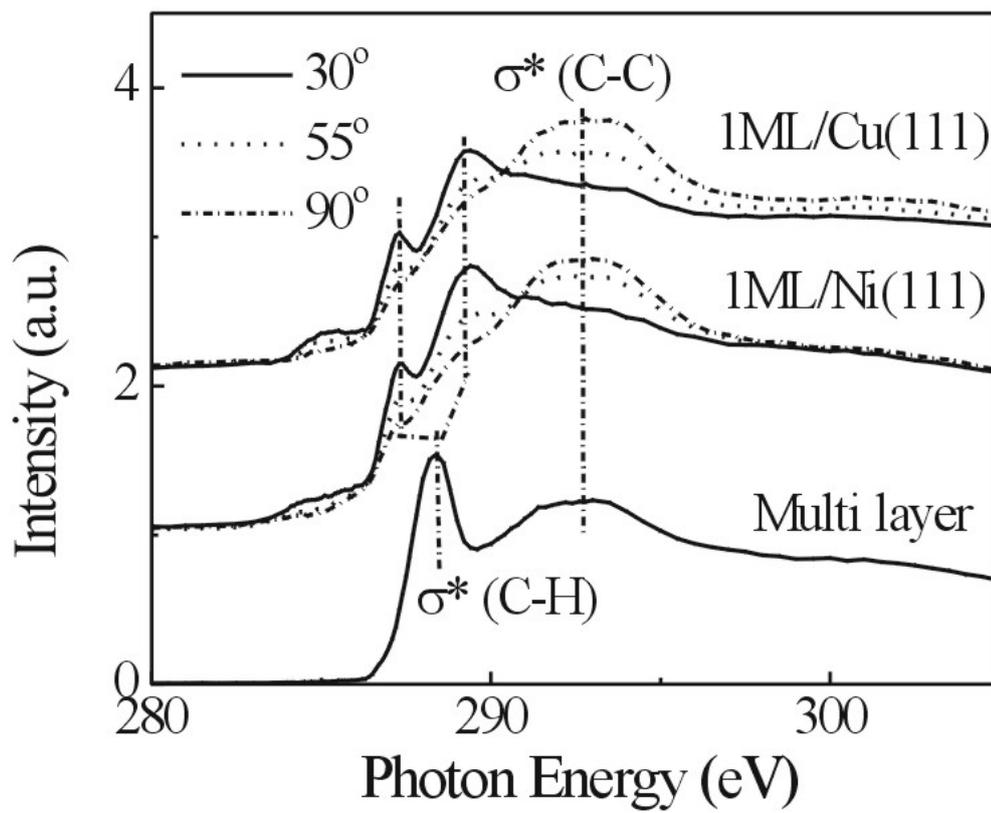


Fig. 2

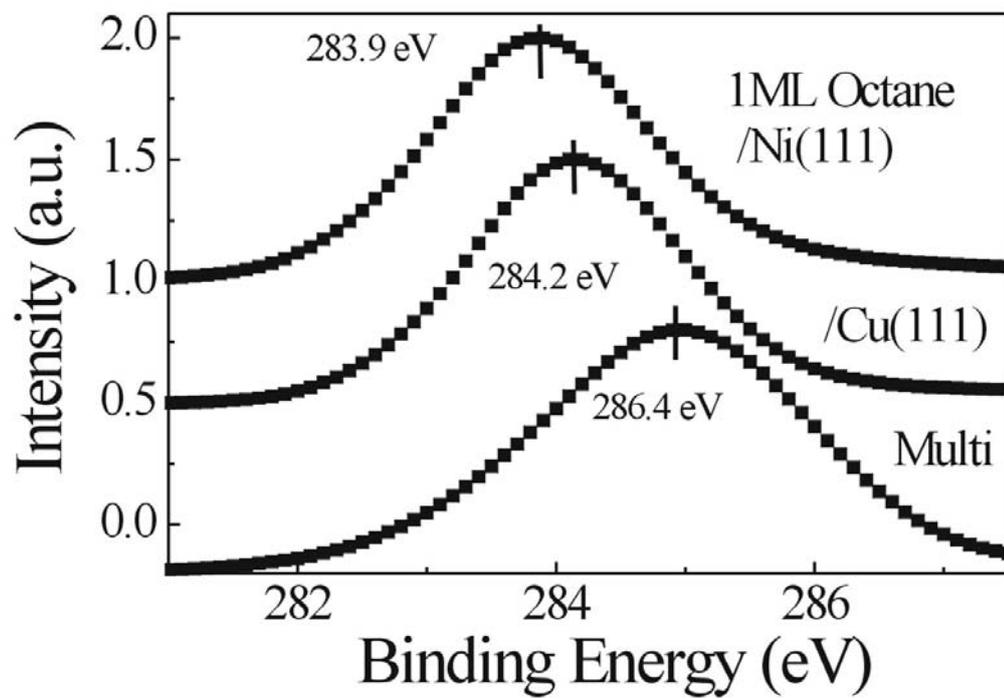


Fig. 3

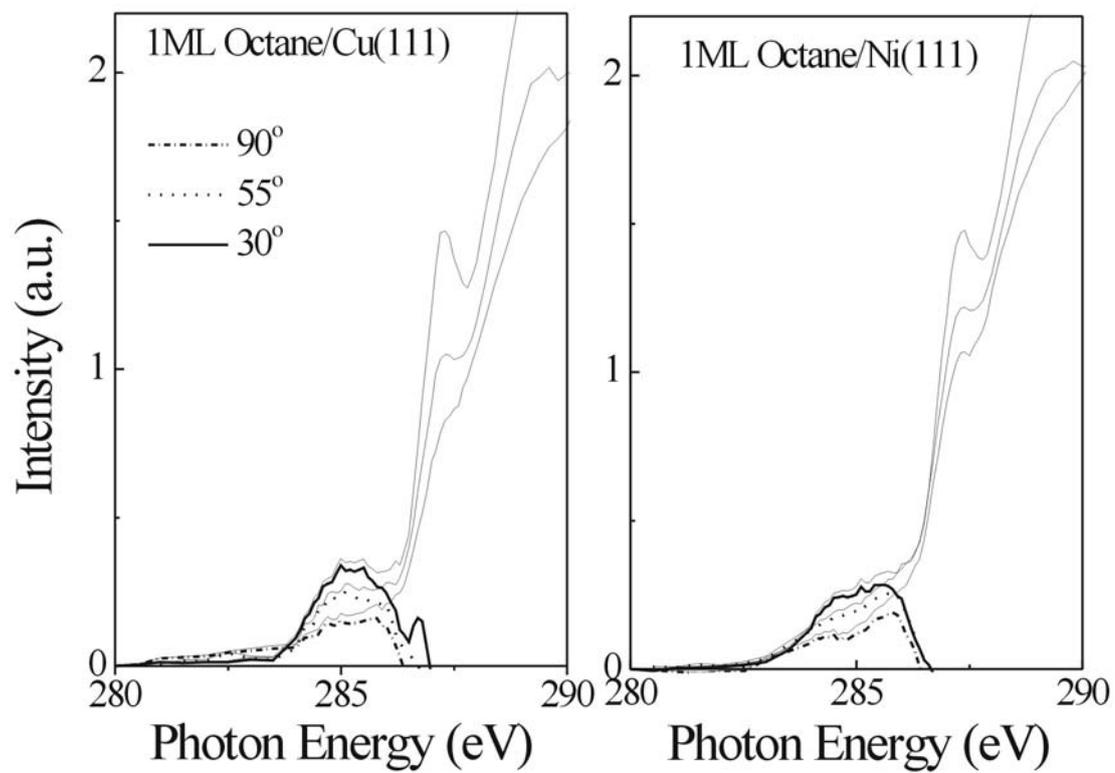


Fig. 4

