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Metal Induced Gap States at Alkali Halide/Metal interface

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Abstract

The electronic state of a KCl/Cu(001) interface was investigated using the Cl *K*-edge near edge X-ray absorption fine structure (NEXAFS). A pre-peak observed on the bulk edge onset of thin KCl films has a similar feature to the peak at a LiCl/Cu(001) interface, which originates from the metal induced gap state (MIGS). The present result indicates that the MIGS is formed universally at alkali halide/metal interfaces. The decay length of MIGS to an insulator differs from each other, mainly due to the difference in the band gap energy of alkali halide.

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Keywords: Metal-insulator interfaces; Near edge extended X-ray absorption fine structure; Alkali halides

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1 Introduction

The electronic structure of insulator/metal interfaces has attracted wide attention in relation to intriguing phenomena, such as band gap narrowing, insulator-metal transition, superconductivity [1,2]. Recently, we have obtained an unambiguous evidence that metal induced gap states (MIGS) are formed at atomically well-defined LiCl/metal interfaces by measuring near-edge x-ray absorption fine structure (NEXAFS) [3]. With a decreasing LiCl thickness, a well pronounced pre-peak appeared at the bulk edge onset in NEXAFS, suggesting formation of a new state in the band gap region. The result of electron spectroscopies (X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES)), and theoretical calculations indicated that the pre-peak on the bulk edge onset originates not from the simple chemical bond but from the proximity of ionic material to metals.

The result of polarization dependent NEXAFS showed that the MIGS has a p_z like structure, extending its electron cloud along the surface normal (parallel to z-axis). The result of thickness dependent NEXAFS showed the decay length of the MIGS into the insulating side is $2.6(\pm 0.3)$ Å at a LiCl/Cu(001) interface.

Although we have found the novel electronic state, MIGS, at the well-ordered LiCl/metal interfaces, it is not clear whether the MIGS is universally formed at alkali halide/metal system or specific to the LiCl/metal interfaces. In the present work, we have investigated the electronic state in KCl/Cu(001) by NEXAFS and XPS. The polarization and thickness dependent NEXAFS measurements were performed to determine the orientation and the decay length of the interface state. By comparing the decay length between these systems, we would discuss the relation between the band gap energy and the decay length of the MIGS.

2 Experimental

The experiments were performed in a custom-designed ultrahigh-vacuum (UHV) system

with a base pressure of 1×10^{-7} Pa. A mechanically and electrochemically polished Cu(001) crystal was cleaned by repeated cycles of Ar^+ sputtering and annealing at 900 K. After repeated preparation cycles, both S and Cl contaminations were found to be less than 0.01 ML. KCl was evaporated from a Knudsen cell at the substrate temperature of 300 K. The growth rate was monitored using a quartz crystal oscillator, and it was on the order of 1 ML (3.1 \AA) /min. Real-time observation of the film crystallinity was done by reflection high energy electron diffraction (RHEED). Sharp streaks in RHEED patterns were observed for the grown KCl films, indicating that an epitaxial KCl film grew in a layer-by-layer fashion [4].

Cl-K edge NEXAFS measurements were carried out at the soft X-ray double-crystal monochromator station BL-11B of the Photon Factory in National Laboratory for High Energy Physics [5]. The energy resolution of the Ge(111) monochromator was about 1.5 eV around the Cl-K edge region. The fluorescence yield detection method was employed to obtain Cl-K edge NEXAFS data by using an UHV-compatible gas-flow proportional counter with P10 gas (10 % CH_4 in Ar) as a detector [6].

3 Result and Discussion

Figure 1 shows the thickness dependent Cl-K edge NEXAFS spectra of KCl/Cu(001) taken at grazing ($\theta=30^\circ$) X-ray incident angles. All the spectra are normalized by their edge-jump. In the bulk KCl spectrum, various peaks are observed, which are assigned to transitions from Cl 1s to unoccupied Cl-p states or the EXAFS structure. For thin KCl films, a well-pronounced pre-peak (p^*) appears on the bulk edge onset. The intensity of the pre-peak increases with decreasing KCl thickness. The appearance of p^* suggests the formation of MIGS at the KCl/Cu(001) interface, as is the case with LiCl/Cu(001) [3].

To confirm whether the chemical state of Cl in the KCl film is modified or not, we investigated the electronic structure of the KCl film with XPS. Figure 2 shows the thickness

dependent Cl 1s XPS of KCl/Cu(001). For comparison, the spectrum of bulk KCl crystal and the peak position of the bulk CuCl (dot line in the figure) are also measured and indicated. The Cl 1s binding energy of KCl is larger by 3 eV than that of CuCl. If the KCl film interacts with the Cu substrate and forms a new chemical bond at the interface, a satellite peak at the lower binding energy side or the broadening of the peak would occur. However, the FWHM of the Cl 1s peak do not change with film thickness, nor does a satellite peak appear in KCl/Cu(001). These results show that no chemical bond was formed at the interface. Here it should be noticed that the binding energy of Cl 1s decreases by 0.6 eV with decreasing KCl thickness, while that did not change in the case of LiCl/Cu(001). The difference of the binding energy shift between LiCl/Cu(001) and KCl/Cu(001) would be discussed in the later section.

The above NEXAFS and XPS results show that the pre-peak originates not from the local Cl-Cu bonds at the KCl/metal interface, but from the states formed by the proximity of an ionic compound to a metal. Therefore, the state can be qualitatively understood as metal induced gap state (MIGS) [3]. The fact that the MIGS was also observed for KCl/Cu(001) supported that the MIGS was generally formed at the alkali halide/metal interface. MIGS originates from the metal wave functions decaying exponentially into the insulating side of the interface, and has amplitudes at both Cu and KCl.

In order to discuss the character of the MIGS, polarization and thickness dependent NEXAFS spectra were measured for KCl/Cu(001). Figure 3 shows the polarization dependent NEXAFS result of the 1 ML thick KCl film. The intensity of the pre-peak is larger for the grazing x-ray incidence, indicating that the MIGS had a p_z like structure, as is the case with the previous LiCl/Cu(001) case [3].

Next, we evaluated the decay length of the MIGS of KCl/Cu(001) by thickness dependent NEXAFS. The decay length (λ) was estimated according to the following procedure [3]. First, the pre-peak of the n ML film was extracted by subtracting the bulk component. Figure 4 shows the intensity of the pre-peak (not normalized by edge-jump) as a

function of film thickness. Assuming that the density of the MIGS at distance x could be represented as $f(x) = I_0 \exp(-x/\lambda)$ and probing depth of NEXAFS is around 10000 Å, the intensity of the MIGS of the n ML film ($F(n)$) was obtained by integrating $f(x)$ from 0 to $na/2$, where I_0 and a were the intensity of the MIGS at the interface and lattice constant. Thus, $F(n)$ was described by $I_0\lambda(1 - \exp(-na/2\lambda))$. By fitting the experimental data in Fig. 4 with $F(n)$, λ was determined to be $4.6(\pm 0.5)$ Å. The result for the fitting is included in Fig. 4.

We then compare the decay length of the MIGS between KCl/Cu(001) and LiCl/Cu(001). λ is $2.6(\pm 0.3)$ Å and $4.6(\pm 0.5)$ Å for LiCl/Cu(001) and KCl/Cu(001), respectively. Theoretical calculation shows that the MIGS is localized at the interface for a wide gap semiconductor [7]. The penetration depth of MIGS to the insulator can be discussed in terms of a finite square-well potential problem. The penetration depth of wave function is proportional to $V^{-\frac{1}{2}}$, where V is the height of the potential well. In the present insulator/metal systems, V corresponds to the energy difference between the Fermi level and the bottom of the conduction band. Since V increases with an increasing energy gap, the penetration depth of the wave function (MIGS) increases with a decreasing energy gap. The band gap energy is 8.5 eV and 9.4 eV for KCl and LiCl, and, thus, λ was larger for KCl/Cu(001) than LiCl/Cu(001).

Finally, the chemical shift of Cl 1s peak in XPS would be discussed in terms of the MIGS. The MIGS is thought to originate from metal wave functions whose (exponential) tails penetrate into the insulating side of the interface. The above discussion showed that the penetration of the metal wave function (electron) is larger for KCl/Cu(001) than LiCl/Cu(001), and thus the density of electron at the Cl atom would be larger for the former case than the latter case. The larger electron density at Cl sites would cause the decrease of Cl 1s binding energy in KCl/Cu(001), while there was no chemical shift in LiCl/Cu(001) even for the thinnest film.

4 Conclusion

We have studied the electronic structure of KCl/Cu(001), comparing with our previous study of LiCl/Cu(001). The MIGS was also observed for KCl/Cu(001), indicating that the MIGS was generally formed at the alkali halide/metal interface. The XPS for thin KCl films showed a decrease in binding energy of Cl 1s for thin films, while there was no chemical shift in LiCl/Cu(001). The decay length (4.6 Å) of the MIGS in KCl/Cu(001) was larger than that (2.6 Å) in LiCl/Cu(001) because of the difference of band gap energy of alkali halides.

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Figure captions

Fig. 1: Thickness dependent Cl-*K* edge NEXAFS spectra for the KCl film grown on Cu(001). The X-ray incidence angle was 30°. All the spectra are normalized by their edge-jump.

Fig. 2: The Cl 1s XPS spectra in KCl/Cu(001) for various thicknesses of the KCl layer with a photon energy of 2900 eV. The binding energies are defined with respect to the Fermi level. For comparison, the binding energy of the bulk CuCl crystal is shown in the figure.

Fig. 3: Polarization dependence of the Cl-*K* edge NEXAFS spectra for 1 ML KCl/Cu(001).

Fig. 4: The intensity of the pre-peak (not normalized by the edge-jump unlike in Fig. 1) versus the film thickness, where the curves are the least-square fitting to $F(n)$. The intensity of the pre-peak for the KCl film was obtained by subtracting the bulk component from the spectra. For comparison, the result of LiCl/Cu(001) is also shown in the figure.

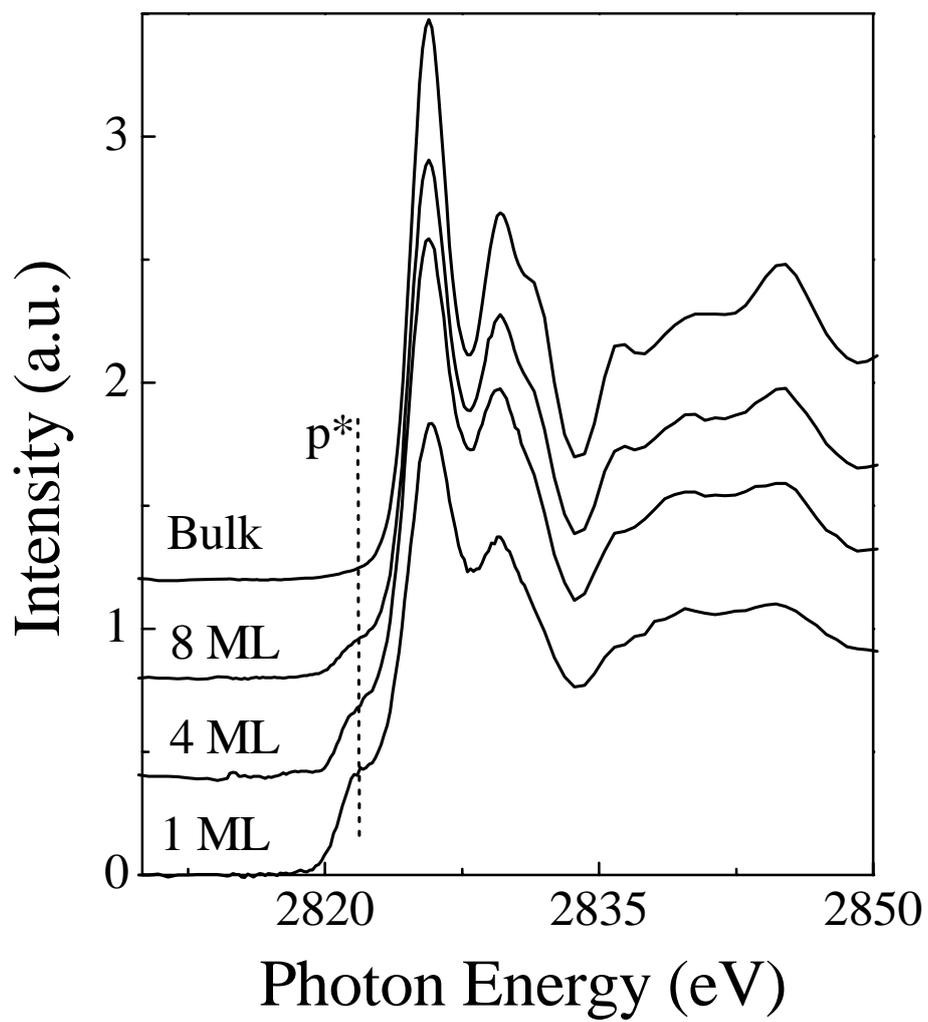


Fig. 1

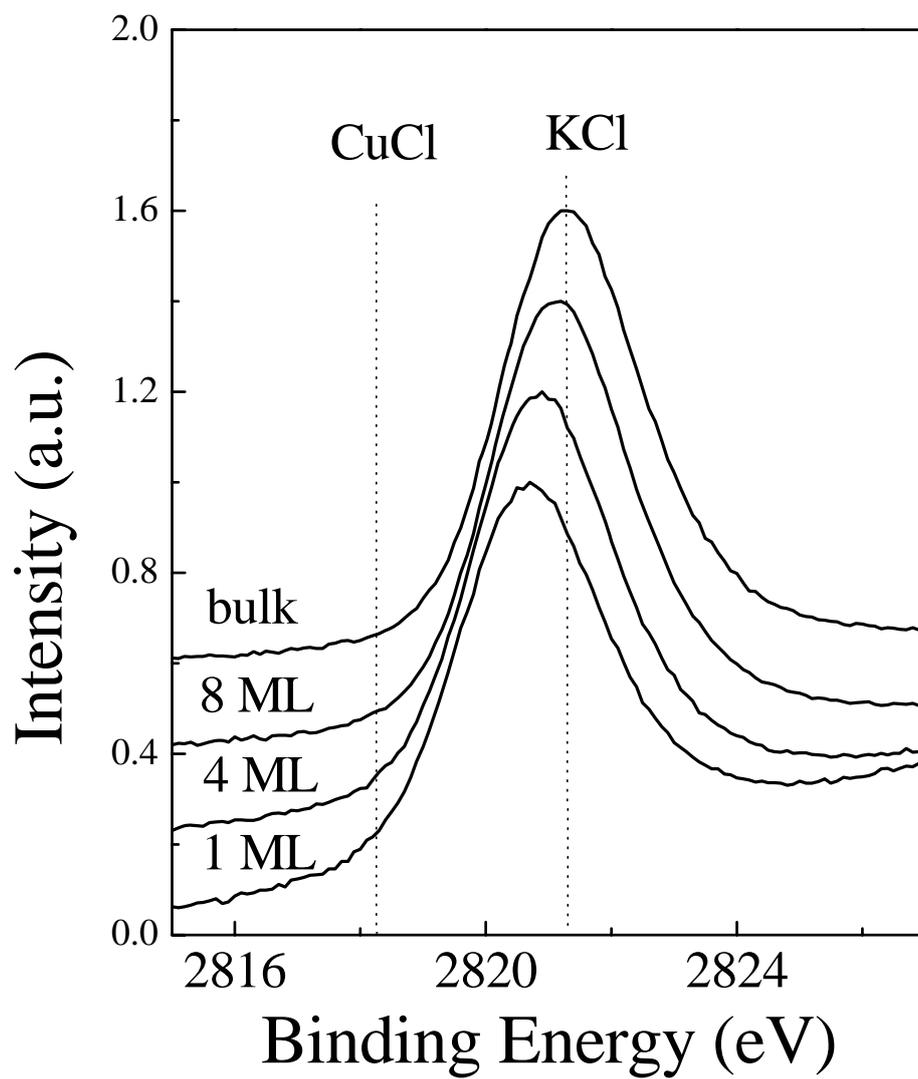


Fig. 2

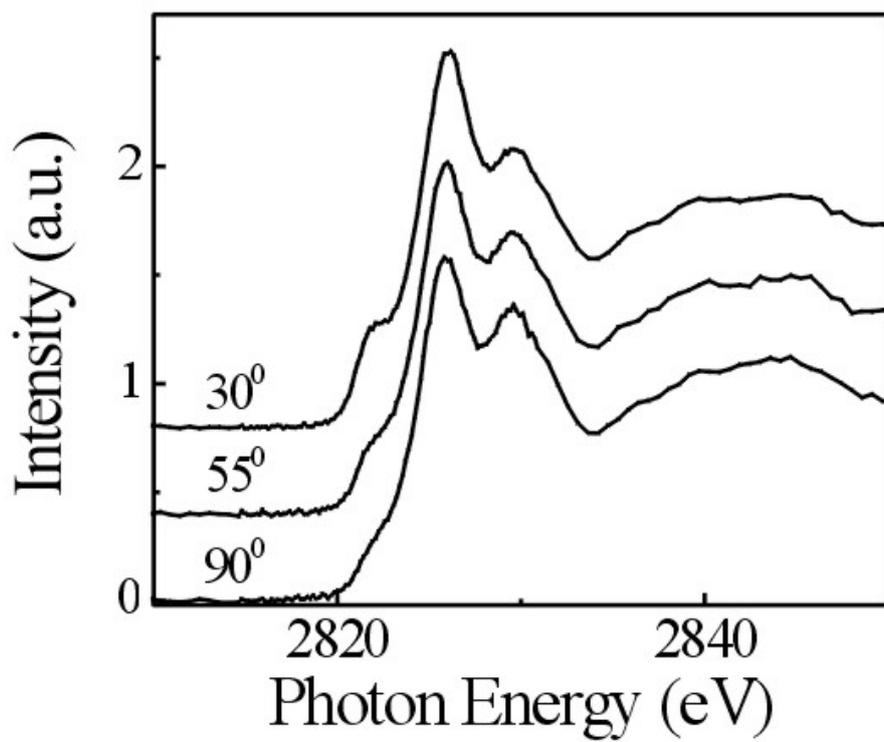


Fig. 3

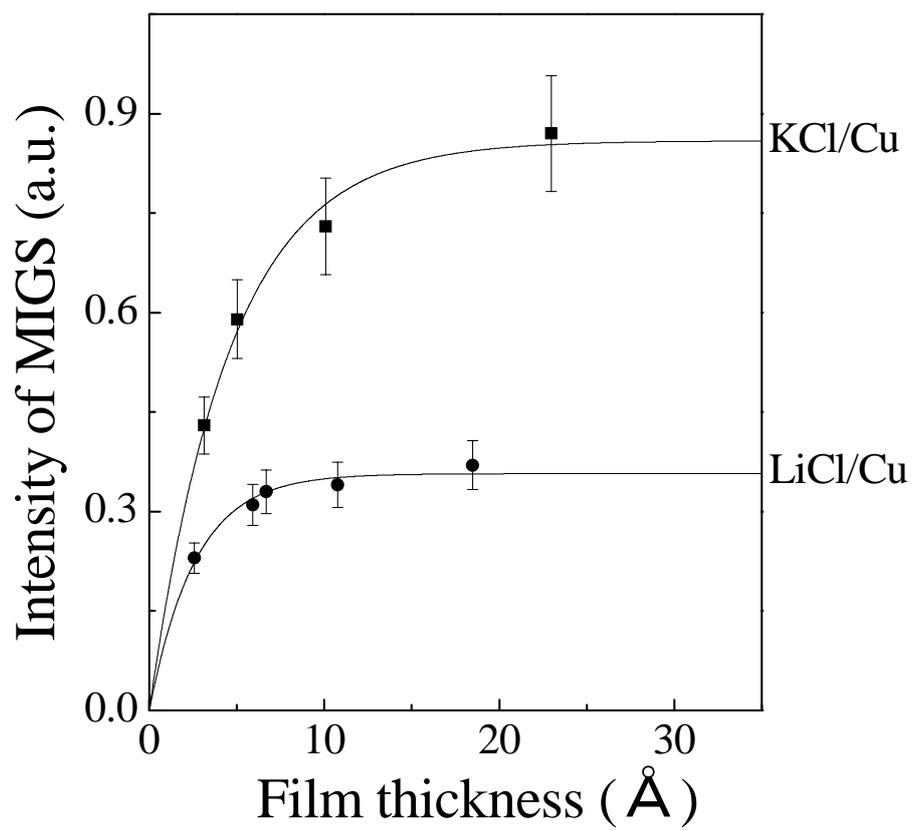


Fig. 4