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Electronic properties of metal-induced gap states formed at alkali-halide/metal interfaces

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The spatial distribution and site distribution of metal-induced gap states (MIGS) are studied by thickness-dependent near-edge x-ray absorption fine structure (NEXAFS) and by comparing the cation and anion-edge NEXAFS. The thickness-dependent NEXAFS shows that the decay length of MIGS depends on an alkali-halide rather than a metal, and it is larger for alkali-halides with smaller band gap energies. By comparing the Cl-edge and K-edge NEXAFS for KCl/Cu(001), MIGS are found to be states localizing at anion sites.

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The electronic structure of semiconductor/metal or insulator/metal interfaces has attracted wide attention in relation to intriguing phenomena, such as band-gap narrowing, insulator-metal transition, and excitonic superconductivity.[1–3] One of the characteristic electronic structures at the interfaces is the formation of a metal-induced gap state (MIGS). At the semiconductor (or insulator)/metal interface, a free-electron-like metal wave function penetrates into a semiconductor (or insulator) side, and thus, an interface electronic state (MIGS) is formed in the band gap.[4] The MIGS has been considered to determine the Schottky barrier height at the semiconductor/metal interface.[5]

While the decay length of the MIGS is an order of a few angstroms for typical semiconductors, it has generally been believed that the decay length of the MIGS into the insulator is negligible. This view is based on quite a plausible tight-binding model calculation.[6] For a typical ionic insulator such as LiCl with a band gap of 9.4 eV, the decay length is estimated to be smaller than 0.1 nm, which suggests that MIGS should be irrelevant at the insulator/metal interface. However, we have obtained unambiguous evidence that the MIGS are formed at atomically well-defined LiCl/metal interfaces by measuring the near-edge x-ray absorption fine structure (NEXAFS).[7–9] With a decreasing LiCl thickness, a well pronounced prepeak appears at the bulk-edge onset in NEXAFS, suggesting the formation of an interface state in the band gap. The results of electron spectroscopies (x-ray photoemission spectroscopy and Auger electron spectroscopy) and theoretical calculation indicate that the prepeak originates not from the simple chemical bond, but from the proximity of ionic material to metals. Furthermore, it has been revealed that the decay length of the MIGS is as large as 0.3 nm and that the MIGS have a p_z-like structure, extending their electron clouds along the surface normal direction (parallel to the z axis).

Although we have reported the existence of MIGS at the LiCl/metal interface, there still remain points to be discussed. First, the decisive factor to determine the decay length of the MIGS is not clear at the alkali-halide/metal interface. What is the decisive factor: metal substrates, alkali-halides, or their combinations? Second, it is not clear whether the MIGS extend uniformly in the surface parallel direction or if they are localized at the anion or cation site.

In order to determine the decisive factor, we have measured the NEXAFS for KCl/metal and discussed the decay length of the MIGS at the alkali-halide/metal interface by comparing the previous LiCl/metal results. To determine the site distribution of the MIGS, we have studied K-edge and Cl-edge NEXAFS for KCl/metal systems. The NEXAFS qualitatively provides information on the unoccupied p electronic density of states of the x-ray absorbing atom. By comparing the intensity of the MIGS peak in K-edge and Cl-edge NEXAFS for KCl/metal, the density of states of the MIGS at the K and Cl sites are evaluated. Therefore, we can discuss whether the MIGS extend uniformly in the surface parallel direction or if they are localized at the anion or cation site. Finally we comment on the possibility of interface superconductivity.

The experiments were performed in a custom-designed ultrahigh-vacuum (UHV) system with a base pressure of 1×10^{-7} Pa. Mechanically and electrochemically polished Cu(001) and Ag(001) crystals were cleaned by repeated cycles of Ar sputtering and annealing at 900 K. 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 (0.31 nm)/min. Real-time observation of the crystallinity of the KCl films was done by reflection high-energy electron diffraction (RHEED). Sharp streaks were observed in the RHEED patterns of the grown KCl films, indicating that an epitaxial KCl(001) film grew in a layer-by-layer fashion.[7,8]

Cl-K-edge and K-K-edge NEXAFS measurements were carried out at the soft x-ray double-crystal monochromator station BL-11B of the Photon Factory in the High Energy Accelerator Research Organization.[10] The energy resolution of the Ge(111) monochromator was about 1.5 eV. The fluorescence-yield detection method was employed to obtain NEXAFS data by using an UHV-compatible gas-flow proportional counter with P10 gas (10% CH_4 in Ar) as a detector. The Cl 1s x-ray photoemission spectrum (XPS) was measured using x-ray synchrotron radiation at 2900 eV with a RIGAKU XPS-7000 concentric hemispherical analyzer. In the XPS for KCl/metal systems, the width of the Cl 1s peak does not change with the film thickness, nor does a satellite

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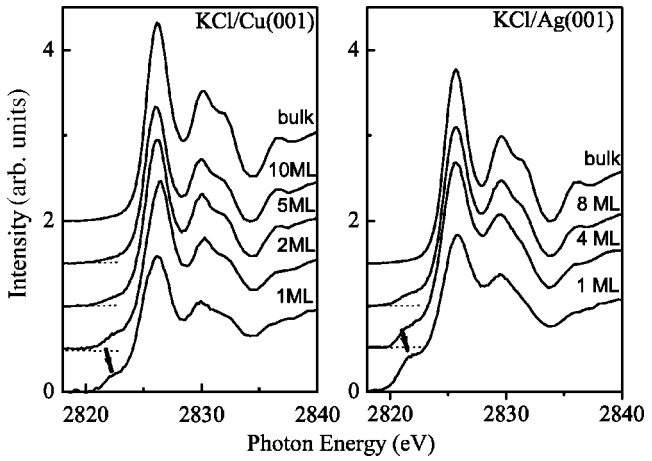

FIG. 1. The Cl-*K*-edge NEXAFS spectra of KCl films grown on Cu(001) and Ag(001) for various thicknesses of the KCl layer taken at the x-ray incidence angle of 15°. All of the spectra are normalized by their edge jumps.

peak appear, indicating that a chemical bond (Cl-Cu or Cl-Ag bonds) is not formed at the KCl/metal interface.

Figure 1 shows the Cl-*K*-edge NEXAFS for the epitaxially grown KCl film on Ag(001) and Cu(001) taking at grazing x-ray incidence (15°) for various thicknesses of the KCl layer. All the spectra are normalized by their edge jumps. In the thin film region, a well pronounced prepeak, which originates from the MIGS, appears just below the bulk-edge onset. In the following, we will discuss the spatial distribution of the MIGS at the alkali-halide/metal interface by analyzing the intensity of this prepeak.

First, the spatial distribution of the MIGS in the surface normal direction is discussed in terms of the decay length of the MIGS. Figure 2 shows the intensity of the prepeak (not normalized by the edge jump unlike in Fig. 1) as a function of the film thickness. Here, we assume that the probing depth of the NEXAFS is much greater (typically $\geqslant 1000$ nm) than the atomic scale, and the intensity of the MIGS $[f(x)]$ at the distance x from the interface can be represented as $I_0 \exp(-x/\lambda)$, where I_0, x, and λ are the intensity of the MIGS at the interface and decay length, respectively. The intensity of the MIGS $[F(X)$; film thickness $X]$ observed by

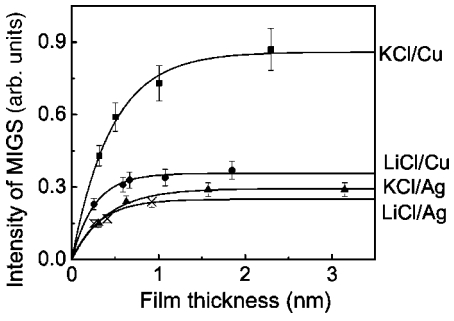

FIG. 2. The intensity of the prepeak (not normalized by the edge jump, unlike in Fig. 1) versus the film thickness, where the curves indicate the results of the least-square fit to $F(X)$. The intensity of the prepeak for the alkali-halide film was obtained by subtracting the bulk component from the spectra.

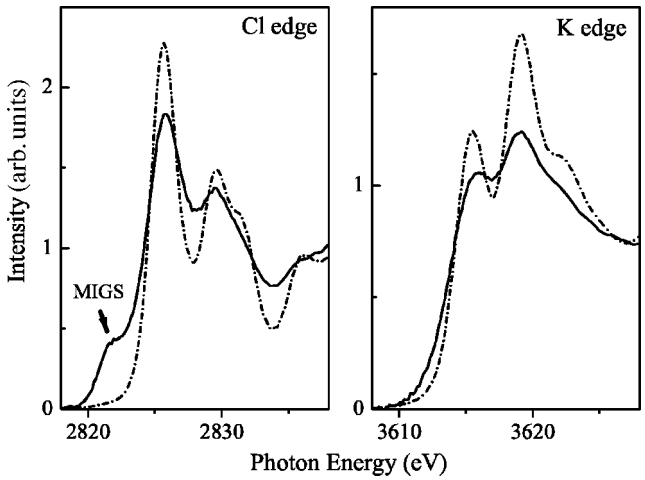

FIG. 3. The Cl-*K*-edge and K-*K*-edge NEXAFS spectra of 1-ML-thick KCl films grown on Cu(001) taken at the x-ray incidence angle of 15° (line), together with the spectra of the bulk KCl (dotted line).

the NEXAFS is thus represented as $I_0\lambda[1-\exp(-X/\lambda)]$ by integrating $f(x)$ from 0 to X. By fitting the experimental data with $F(X)$, the decay length is determined to be 0.46 nm for KCl/Cu(001), 0.41 nm for KCl/Ag(001), 0.26 nm for LiCl/Cu(001), and 0.29 nm for LiCl/Ag(001). The result for the fitting is included in Fig. 2.

The intensity of the MIGS at the interface is 19 (a.u.) for KCl/Cu(001), 7.1 for KCl/Ag(001), 14 for LiCl/Cu(001), and 8.6 for LiCl/Ag(001). It can be found that the decay length of the MIGS depends on the kind of alkali-halide, not on the metal. This conclusion is consistent with the recent theoretical calculation conducted by Arita *et al.*[11] They have evaluated the decay length of the MIGS for various alkali-halide/metal combinations by the *ab initio* calculation, in which they conclude that the decay length of the MIGS is close to half the lattice constant of the alkali-halides. Since the lattice constant of KCl ($L=0.63$ nm) is larger than that of LiCl ($L=0.51$ nm), the present experimental results are consistent with the theoretical calculation results.

In contrast with the decay length, the intensity of the MIGS at the interface depends on the metal substrate. The intensity of the MIGS at the alkali-halide/Cu(001) interface (I_0) is larger than that at the alkali-halide/Ag(001) interface. This difference can be explained by the density of states of metal substrates near the Fermi energy. Since the penetration of electrons in the metal causes the MIGS, the intensity of the MIGS at the interface relates closely with the density of states at the Fermi energy, E_F. The density of states at E_F for Cu is larger than that for Ag (r_s parameter: 2.7 for Cu, 3.0 for Ag). It is thus reasonable that the intensity of the MIGS at the alkali-halide/Cu(001) interface is larger than that at the alkali-halide/Ag(001) interface.

In the previous section, we have discussed the spatial distribution of the MIGS in the surface normal direction. We now discuss the spatial distribution of the MIGS in the surface parallel direction. The Cl-*K*-edge and K-*K*-edge NEXAFS provide information on the unoccupied Cl-*p* and K-*p* electronic densities of states. The topmost surface of the

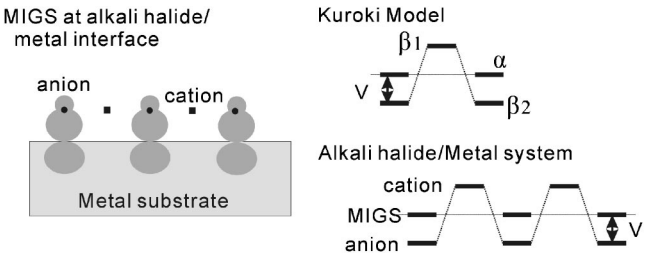

FIG. 4. Systematic view of the MIGS at the alkali-halide/metal interface. The positions of the cation (box) and the anion (circle) are shown in the figure. (Right) Kuroki model and a multiband model of alkali-halide/metal interfaces. In the Kuroki model, the carrier band (α) interacts repulsively with the insulating band (β_2). In the alkali-halide/metal system, the MIGS band interacts with the anion band.

alkali-halide/face-centered-cubic (fcc) metal heterostructures is just the (001) face of the alkali-halide crystal, consisting of the same number of cations and anions. Therefore, we can discuss the site distribution of the MIGS in the surface parallel direction by comparing the intensity of the MIGS peak in both Cl-edge and K-edge NEXAFS for the KCl/metal system. Figure 3 shows Cl-*K*-edge and K-*K*-edge NEXAFS for the 1-ML-thick KCl film on Cu(001). The prepeak originating from the MIGS is clearly observed at the Cl edge, while the prepeak is not observed at the K edge, indicating that the MIGS are formed only at the anion site. On the other hand, the polarization-dependent NEXAFS results show that the MIGS are the states extending their electron clouds along the surface normal direction.[9] Considering these NEXAFS results and our previous calculation results (Fig. 3 in Ref. 9), we can present a systematic view of the spatial distribution of the MIGS for the alkali-halide/metal interface as seen in Fig. 4.

The localization of the MIGS at the anion site can be discussed by considering the calculation results done by Arita *et al.*[11] Generally, the MIGS can be divided into two groups: one having a conduction-band character and the other having a valence-band character at the insulator side of the interface. Noguera and Bordier introduced the energy E_{ZCP} which categorizes the character of the MIGS.[6] According to their theory, an electronic state has a conduction-band character when its electronic energy is larger than E_{ZCP}, and vice versa. On the other hand, the charge transfer between the insulator and the metal is determined by the energy position of E_{ZCP} relative to the Fermi energy (E_F). The charge is transferred from the insulator to the metal, if $E_{ZCP} > E_F$. Arita *et al.* evaluate the charge transfer for various alkali-halide/metal combinations by *ab initio* calculations, and find that the charge transfer from the insulator to the metal commonly occurs for the alkali-halide/metal systems.[11] This indicates that E_{ZCP} is higher than E_F for the alkali-halide/metal systems, and thus, the electronic state near E_F has a valence band character. Since the MIGS are electronic states formed near E_F, the MIGS have a valence band character, and they are localized at the anion site.

Finally, let us point out that the electronic structure specific to the alkali-halide/metal interfaces can have implications for superconductivity. In the previous study, we propose a possibility of the MIGS working favorably for exciton-mediated superconductivity.[9,11] In the presence of the MIGS at the alkali-halide/metal interface, an exciton [associated with the wide-band gap of the alkali-halide] and carriers (from the MIGS) coexist within one atomic distance, a situation which is favorable for strong interaction between the carriers and the exciton. This strong interaction leads to a possible ground for superconductivity by the exciton mechanism proposed by Ginzburg *et al.*[3]

The localization of the MIGS at the anion sites provides another possibility of superconductivity proposed by Kuroki and Aoki.[12] They propose that repulsively interacting systems consisting of a carrier band and an insulating band can become superconducting, and the system can be effectively mapped to an attractive Hubbard model. In their model, the metallic band is assumed to interact only with the anion sites (or the cation sites). Figure 4 shows the Kuroki model, where the carrier band (α) interacts repulsively (V) with the insulating band (β_2). At the alkali-halide/metal interface, the MIGS have their amplitudes only on the anion sites, so that the MIGS should interact primarily with the anion sites, which just corresponds to the situation considered in Kuroki model. The β_1, β_2, and α bands in the Kuroki model correspond to the anion, cation, and MIGS bands in the alkali-halide/metal systems, as shown in Fig. 4. So we may envisage that the alkali-halide/metal interface may provide a possible ground for superconductivity, although quantitative prediction for T_c could not be done at the present stage.

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