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Metal-Induced Gap States at Well Defined Alkali-Halide/Metal Interfaces

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In order to search for states specific to insulator/metal interfaces, we have studied epitaxially grown interfaces with element-selective near edge x-ray absorption fine structure. An extra peak is observed below the bulk edge onset for LiCl films on Cu and Ag substrates. The nature of chemical bonds as probed by x-ray photoemission spectroscopy and Auger electron spectroscopy remains unchanged, so we regard this as evidence for metal-induced gap states (MIGS) formed by the proximity to a metal, rather than local bonds at the interface. The dependence on the film thickness shows that the MIGS are as thin as one monolayer. An *ab initio* electronic structure calculation supports the existence of the MIGS that are strongly localized at the interface.

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Introduction.—While there is mounting interest in the nature of the “heterointerface” (solid-solid interfaces between very dissimilar materials), insulator/metal interfaces are especially intriguing, since they provide fascinating possibilities such as metal-insulator transition [1], band gap narrowing [2], and superconductivity [3], as well as technological possibilities such as catalysis, etc. Despite the interest, electronic structures characteristic of the insulator/metal interface have not been studied satisfactorily, for good reasons. First, well defined interfaces are hard to prepare due to the different nature of chemical bonds. Second, signals from the interface are obscured by significant contribution from the substrate in conventional experimental methods such as ultraviolet photoemission spectroscopy (UPS), inverse photoemission spectroscopy, or electron energy loss spectroscopy (EELS).

Recently, an interesting experimental result was reported for insulator/metal systems. Muller *et al.* studied {222}MgO/Cu interfaces in fine particles (rather than in a film) with transmission EELS, and succeeded in observing metal-induced gap states (MIGS) for the first time [4]. The concept of MIGS was first introduced for semiconductor/metal junctions in discussing the Schottky barrier at the interface [5], and subsequently applied to insulator/metal interfaces [6]. MIGS are thought to accompany metal wave functions whose (exponential) tails penetrate into the insulating side of the interface. Schintke *et al.* studied MgO/Ag(001) with scanning tunneling spectroscopy and found a state in the band gap [7]. However, the first point raised above remains: Since {222}MgO is a polar (hence presumably metallic) surface, whether the prepeak observed for {222}MgO/Cu originates from the polar surface or from the MIGS has not been definite, although their study is pioneering. Further-

more, {222} MgO/Cu is not a well defined interface due to a large lattice mismatch. For MgO/Ag(001), the strong hybridization between the O 2*p* band and the Ag 5*sp* band is expected to dominate the interface [8]. All these should obscure the identification of the MIGS in its proper sense, i.e., states formed solely by the proximity to a metal rather than by local bonds.

In order to clarify this, we propose here to prepare well defined interfaces by exploiting our studies, in which we have revealed that some alkali halides grow heteroepitaxially on metal substrates in a layer-by-layer fashion, so we end up with *atomically well defined insulator/metal interfaces* [9]. Being epitaxially grown, the number of atomic layers can also be controlled, which helps to probe the nature of the interface state. In a previous study we have examined the epitaxially grown LiCl/Cu(001), but were unable to find an indication for the interface state [10], presumably because the methods employed (UPS and EELS) pick up signals from the substrate.

Here we adopt near edge x-ray absorption fine structure (NEXAFS) to study electronic structures at the LiCl/metal interfaces, where the second point raised above comes in. Namely, we adopt Cl-K edge NEXAFS, which is based on x-ray absorption by Cl atoms, and hence provides information on the LiCl film with negligible influences of the substrate. Furthermore, NEXAFS, with its high-energy photons, can probe very deep interfaces, so suited for obtaining the dependence of the interface states on the thickness of the insulating layer.

The results obtained here for LiCl thin films on Cu(001) and Ag(001) indeed exhibit clear evidence for the electronic states intrinsic to the insulator/metal interface which are as thin as one monolayer (ML) [1 ML = 2.6 Å]. We have then compared the experimental result with an *ab initio* density functional calculation, which

supports the existence of the MIGS that are strongly localized at the interface.

Experimental.—Epitaxial LiCl films were grown on metals at 300 K by a Knudsen cell. Cl-*K* edge NEXAFS was carried out at BL-11B in the Photon Factory in Institute of Materials Structure Science [11]. The Cl-*K* NEXAFS provides information on the unoccupied Cl-*p* states[12].

Figure 1 shows the Cl-*K* edge NEXAFS spectra for LiCl/Cu(001) and LiCl/Ag(001) taken at grazing x-ray incidence (15°) for various thicknesses of the LiCl layer. All the spectra are normalized by their edge jumps. Two NEXAFS peaks are observed at 2827 eV (*p*1) and 2829 eV (*p*2) for bulk LiCl. Now, a new finding here is that a pronounced prepeak (*p*3) appears just below the bulk edge onset, which is clearly visible for thinner LiCl layers. Hereafter we will focus on the prepeak.

There are two points to note. First, the prepeak exists even for a 10 ML LiCl on Cu(001). Namely, although the peak may seem more prominent with decreasing the film thickness in Fig. 1, this is an artifact of normalizing the curve by the edge jump. As we shall elaborate in Fig. 1(c), the prepeak appears at 1 ML and its intensity rapidly saturates. Second, the prepeak is observed for both LiCl/Cu(001) and LiCl/Ag(001). For LiCl/Cu(001), LiCl grows with the [100] axis rotated by 45° away from that of the Cu substrate, where both Li and Cl atoms sit on the fourfold hollow sites due to matched Li-Cl and Cu-Cu distances. On the other hand, LiCl on Ag(001) grows without an azimuthal rotation, for which a commensurate structure becomes impossible [9]. Despite the difference in the interface structure between Cu and Ag, the prepeak is observed in both systems, which

precludes local structures at the interface as the origin of the prepeak.

We next confirm whether the nature of chemical bonds is modified around the interface by making use of x-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES). For LiCl/Cu(001), the Cu MMM Auger peak does not shift from that of the clean Cu(001) within 0.1 eV, which implies that the interfacial Cu atoms remain almost neutral [13]. Figure 2 shows the Cl 1*s* XPS spectra for LiCl/Cu(001) for various thicknesses of LiCl. For comparison, the spectrum for a bulk LiCl crystal and the peak position of a bulk CuCl crystal are also measured, which shows that the Cl 1*s* binding energy in LiCl is larger by 2 eV than that of CuCl. If the LiCl film interacted with the Cu substrate to form new chemical bonds at the interface, a satellite peak at the lower binding energy side or the broadening of the peak would arise. However, both the binding energy and the width of the Cl 1*s* peak do not change with the film thickness, nor does a satellite peak appear in LiCl/Cu(001). These show that the chemical state of Cl in LiCl/Cu(001) is virtually the same as that of bulk LiCl with no chemical bonds formed at the interface. Similar results are obtained from Cl 1*s* XPS spectra for LiCl/Ag(001).

Given the above NEXAFS, XPS, and AES results indicating that the prepeak does not originate from chemical bonds at the LiCl/metal interface, the gap states arise from the proximity to a metal, so we can regard them as MIGS. We can also note that the position of the Fermi

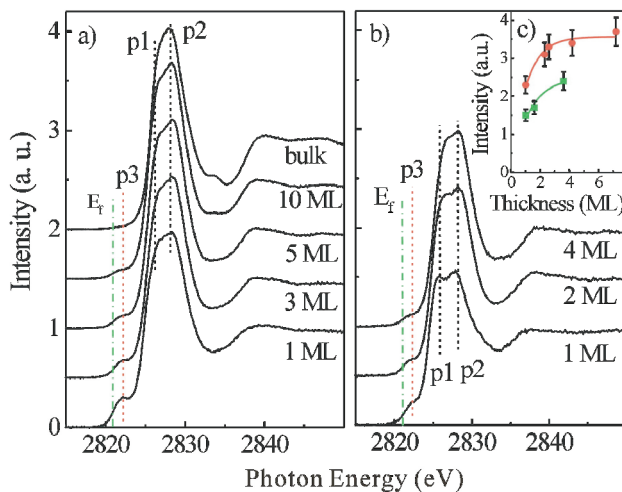


FIG. 1 (color). The Cl-*K* edge NEXAFS spectra in LiCl films grown on (a) Cu(001) and (b) Ag(001). E_F indicates the position of the Fermi level as determined from XPS. The inset (c) shows the intensity of the prepeak (not normalized by the edge jump unlike in the main panel) versus the film thickness, where the curves are the least-squares fit.

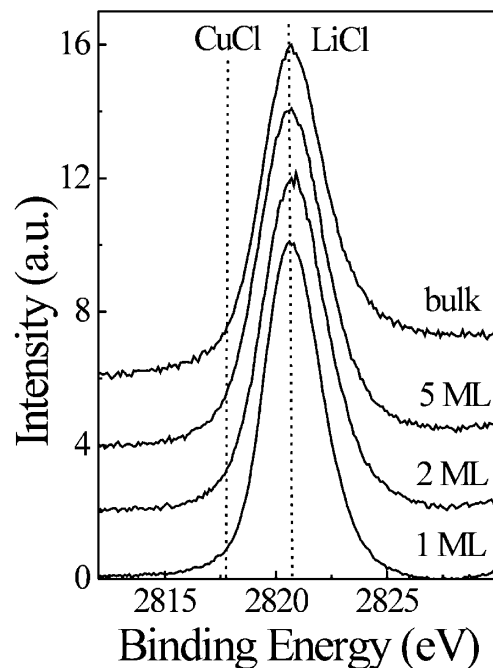


FIG. 2. The Cl 1*s* XPS spectra in LiCl/Cu(001) with a photon energy of 2900 eV. The binding energies are defined with respect to the Fermi level, where the binding energy of the bulk CuCl is also indicated.

level, which can be estimated from the binding energy of Cl $1s$ XPS spectra as indicated in Fig. 1, is seen to be located right in the prepeak. So a finite density of states at E_F implies that LiCl is *metallized* at the interface.

Let us discuss the character of the MIGS in more detail from the NEXAFS data. First, we can exploit the epitaxy-grown samples to estimate the decay length of the MIGS into the insulating side from the dependence of the intensity of the prepeak on the thickness of the insulating layer. Since the probing depth of NEXAFS is orders of magnitude greater (typically $\geq 10\,000$ Å) than the atomic scale, NEXAFS intensity should directly reflect the decay of the MIGS into the insulator. If we assume an exponential decay to fit the experimental data, we end up with the decay length 2.6 ± 0.3 Å for LiCl/Cu(001) and 2.9 ± 0.7 Å for LiCl/Ag(001) [Fig. 1(c)], so the MIGS are indeed localized within a few Å (approximately as small as one monolayer) of the interface.

Second, we have probed the geometry of the MIGS wave function from the polarization dependence of NEXAFS. The prepeak has turned out to be greater for grazing x-ray incidence (Fig. 3), which clearly shows that the MIGS are p_z ($z \perp$ surface)-like[14].

Ab-initio calculation.—Formation of MIGS with a thickness ~ 1 ML is theoretically intriguing, since a simple model for the interface (e.g., tight-binding insulator/jellium) would predict a negligible ($\ll 1$ ML) penetration (for the gap of the insulator $\sim$ several eV)

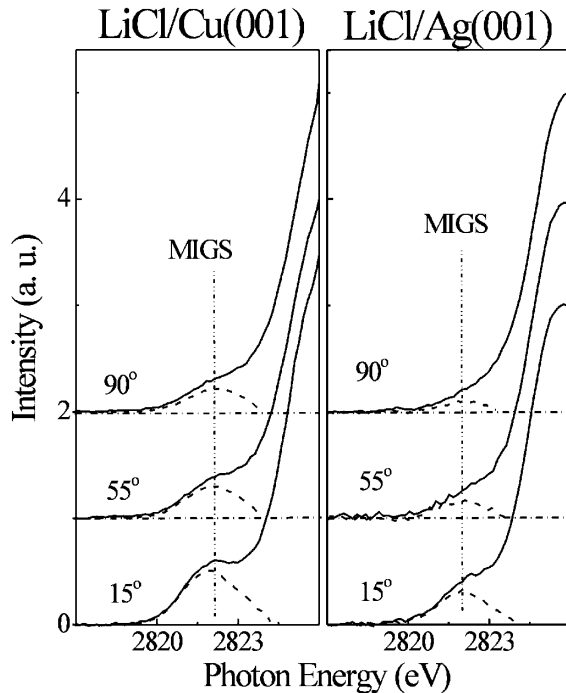


FIG. 3. Polarization dependence of the Cl- K edge NEXAFS spectra for 1 ML LiCl/Cu(001) and 1 ML LiCl/Ag(001). The MIGS-derived peaks (difference between the spectra for bulk LiCl and LiCl/Cu) are indicated by dotted lines.

and would completely fail. So we have performed a first-principles calculation based on the local density functional theory (LDF) with pseudopotentials and plane-wave basis. We have adopted two models, one for LiCl/Cu(001) and the other for LiCl/jellium, to examine whether the MIGS come from the specific metallic substrate (copper here) or a general property of the proximity to an electron gas. The calculation for LiCl/Cu is performed on periodically repeated slabs with five Cu layers sandwiched from top and bottom by one LiCl layer each with the slabs separated by a vacuum of height 50 Å. The in-plane unit cell contains two Cu atoms and one LiCl, which is a virtue of the commensurate structure.

Figure 4(a) shows the band structure of 1 ML LiCl/Cu(001). For comparison we have also obtained the band structure of an isolated 1 ML LiCl film without the metallic substrate. The isolated LiCl has a large band gap, although the size of the gap is, as usually the case with LDF, underestimated by 2–3 eV. When the 1 ML LiCl is put on Cu(001), new bands appear in the gap. We have characterized their nature by looking at the amplitude of the LDF wave functions.

If we look at the three states just above E_F at Γ point, the two in-gap bands closest to E_F have indeed amplitudes that are localized at the interfacial Cl and Cu atoms [Fig. 4(b)]. Existence of such states is, theoretically, remarkable given the fact that LiCl is a very good insulator. They are p_z -like, in agreement with the polarization dependence seen in NEXAFS. Thus we identify that the MIGS observed by NEXAFS should correspond to these states.

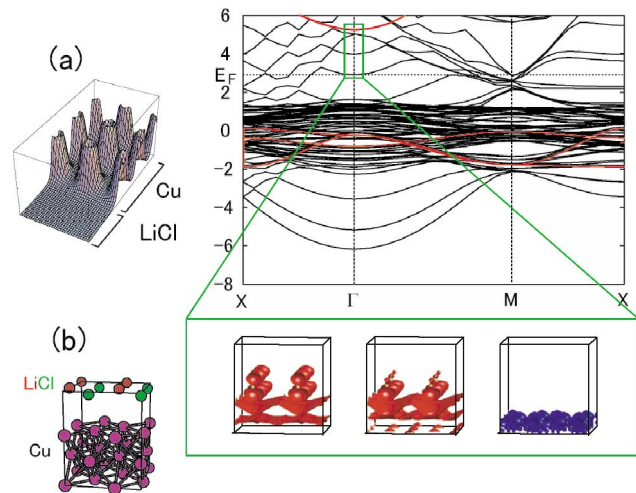


FIG. 4 (color). (a) The band structure of 1 ML LiCl/Cu(001) (black) as compared with that for an isolated 1 ML LiCl (red). (b) Contours of the absolute value of the LDF wave functions for the in-gap states (in the ascending order of energy, enclosed in green), along with the atomic configuration. The wave functions having amplitudes on both Cl and Cu atoms are shown in red. The top-left inset shows the charge distribution difference between LiCl/Cu(001) and an isolated LiCl.

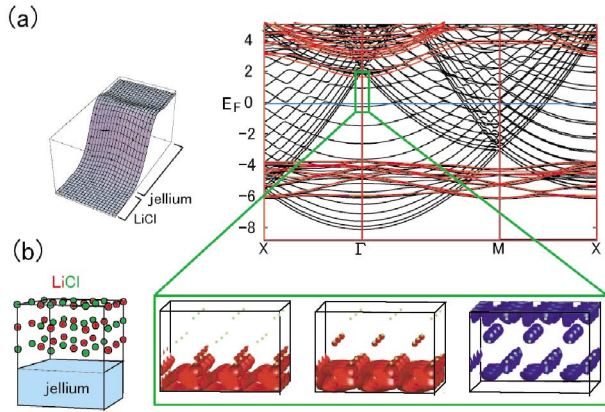


FIG. 5 (color). (a) The band structure of 3 ML LiCl/jellium with $r_s = 2.5$ (black) as compared with that for an isolated 3 ML LiCl (red). (b) Contours of the absolute value of the LDF wave functions, along with the atomic configuration. The wave functions having amplitudes on both Cl and jellium are shown in red. The top-left inset shows the charge distribution difference between LiCl/jellium and an isolated LiCl.

Another theoretical observation is that the new state is by no means a result of a charge transfer across Cu and LiCl. This can be seen in the inset of Fig. 4, which displays the difference in the charge density between LiCl/Cu(001) and the isolated LiCl film. If there were a charge transfer, the charge difference would have an amplitude on the LiCl side as well, while the result shows that it is entirely confined to the Cu side. The absence of charge transfer can explain the absence of core level shifts at the interface in Cl 1s XPS result (Fig. 2).

In order to theoretically estimate the decay length of the MIGS into the insulator, we have then performed an LDF calculation for 3 ML LiCl attached to a jellium of thickness 80 Å (from top and bottom). The replacement of the Cu substrate with a jellium also enables us to examine whether a simplest possible model for the electron gas would already exhibit MIGS. Figure 5(a) shows the band structure of 3 ML LiCl/jellium, where the jellium has $r_s = 2.5$. We have again new in-gap states whose wave functions [Fig. 5(b)] just extend to the interfacial (i.e., the first layer from the jellium) Cl atoms. This result for LiCl/jellium endorses that (i) MIGS are characteristic of insulator/metal interfaces rather than of local chemical bonds, and (ii) ~ 1 ML penetration depth of the MIGS is rather general.

To systematically confirm how the MIGS appear, we have then varied the density of electrons in the metallic side by varying r_s , which is the sole parameter characterizing the jellium. The LDF result shows that MIGS appear with its penetration depth only weakly dependent on r_s . This accounts for the experimental result that MIGS are observed for both Cu (with $r_s = 2.7$) and Ag ($r_s = 3.0$) substrates.

Finally, let us point out that the electronic structure specific to insulator/metal interfaces can possibly have

interesting implications for superconductivity. Discussions on superconductivity at interfaces have a long history. A well known proposal is by Ginzburg *et al.* [3] for the possibility of superconductivity by exciton mechanism at metal/semiconductor interfaces. The presence of excitons requires a wide-gap insulator, which will, however, prevent the metallic carriers to penetrate into the insulator, so that the coexistence (in real space) of excitons and metallic carriers is difficult. To circumvent this they [3] had to consider a hypothetical density of states that has two closely separated peaks in a wide band gap, where the former are required to enable the carriers in the metallic side to tunnel into the semiconductor side.

By contrast, in the present MIGS in insulator/metal interfaces we automatically have a coexistence of excitations [associated with the wide band gap (≈ 9 eV for LiCl) of the insulator] and carriers. To realize a high T_C we have further to realize strong interaction between the carriers and excitons, which should also be fulfilled due to the penetration of MIGS into the insulating layer. So we may envisage that the insulator/metal interface as discussed here may provide a possible ground for superconductivity.

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