Metal-induced gap states at insulator/metal interfaces

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(Received 29 June 2004; Accepted 16 July 2004; Published 23 July 2004)

Keywords: Near edge extended X-ray absorption finestructure (NEXAFS); Interface states; Epitaxy; Alkali halides; Hetero-junctions

I. INTRODUCTION

The nature of the "heterointerface" (solid-solid interfaces between very dissimilar materials) has become a subject of special interest, since novel atomic and electronic structures appear at the interface. At the interface, one can prepare some metastable crystal structures, which closely imitate those of the substrates rather than the bulk equilibrium phase [1, 2]. The interatomic distance can be elongated as large as ∼10 % in some cases [3, 4]. In the technological side, electronic devices, such as diode, transistor, laser, are based on the heterostructures.

From a historical viewpoint, the heterointerface and its electronic structure have been well studied and understood mainly for semiconductor/semiconductor, semiconductor/metal interfaces. We, thus, first discuss the electronic structures characteristic of the semiconductor/metal interface (cf. band gap narrowing and metal induced gap states), in order to discuss the electronic structure at the insulator/metal interface.

Figure 1 shows the schematic band gap narrowing model proposed by Inksan and Anderson [5-8]. They proposed that the band gap narrowing and the metal-insulator transition can take place at and in the vicinity of the semiconductor/metal interface because of many body effects. Classically, their argument is as follows. When a metal and a semiconductor contact, an electron in the semiconductor feels an image potential, which is the interaction between the particle and its image charge in the metal. This leads to a downward bending of the conduction band and an upward bending of the valence band toward the interface, and the band gap energy of the semiconductor decreases around the interface. Recently, Arita et al. showed that the band gap energy of Si reduces from 1.93 eV to 1.85 eV, when jellium attaches to the Si layer by ab initio calculations based on the density functional calculation [9].

Metal induced gap states (MIGS) were first introduced for semiconductor/metal junctions in discussing the Schottky barrier at the interface [10–12]. Figure 2 shows the schematic view of MIGS. When a metal and a semiconductor contact, metal wave functions penetrate into the semiconductor side. Then, new electronic states, MIGS, are formed in the band gap of the semiconductor. The previous band calculation study for the Si/Al system showed that extra electronic states (MIGS) appear in the band gap of Si at the interface [10]. The formation of MIGS in the band gap of the semiconductor means that a metallic phase appears in the semiconductor. Therefore, when a metal and a semiconductor contact, the chemical potential of this metallic phase in the semiconductor would agree with that of the metal. In other words, MIGS determine the band alignment at the semiconductor/metal interface and Schottky barrier height [11, 12]. Although MIGS are widely discussed in the semiconductor/metal interface, there have been little experiments to detect MIGS, for the following reasons. First, strong chemical bond is formed at the semiconductor/metal interface, and it is hard to distinguish between

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FIG. 1: Schematic band gap narrowing model at the semiconductor/metal interface. The band gap of the semiconductor decreases around the interface because of many body effects.
The electronic structure at the insulator/metal interface, based on the above discussion about the electronic structure of the semiconductor/metal interface. Since the band gap energy of an insulator is wide, it is considered that an electron of a metal does not penetrate into the insulator side, that is, a metal and an insulator would interact weakly. In other words, the electronic structure of an insulator at the interface was thought to be the same as that of bulk. Furthermore, well-defined interfaces are hard to be prepared due to different natures in the chemical bond between insulators and metals. Therefore, the electronic structure at the insulator/metal interface has not been studied satisfactorily.

Recently, however, there has been a growing interest in the insulator/metal interface due to their importance in catalysis, device applications and fundamental science. On the technological side, they are of considerable significance as insulating barriers in miniaturized electronic circuits, and as magnetic tunnel junctions for magneto-electronics and magnetic data storage [13]. The development of molecular beam epitaxy technique has recently made it possible to prepare some well-ordered insulator/metal interfaces, and several interesting results are reported at the interface.

First, the band gap narrowing was reported at the Al2O3/Ru(0001) interface [14]. Murata et al. grew a flat single crystalline Al2O3 film on Ru(0001), and measured thickness dependence of the band gap energy of the Al2O3 film. The band gap energy of the Al2O3 film decreases with decreasing oxide thickness, and they showed the band gap narrowing at the insulator/metal interface.

Second, MIGS was reported at the MgO/Cu interface [15]. Muller et al. prepared MgO/Cu(222) interfaces in thin film by annealing Mg-Cu bimetal, and studied their electronic structure by O-K edge electron energy loss spectroscopy (EELS). A new electronic state was found in the band gap of MgO at the interface, and they assigned this state to MIGS. Although their study is pioneering, their discussion has remained obscure. It is because the MgO(222) surface is a polar surface and the polar surface itself is a metallic surface [16–18]. Furthermore, the interface MgO/Cu is not a well-defined interface because of the large misfit in the lattice constants. All these should obscure the nature of the interface states. Thus the MIGS in its proper sense, i.e., those originating from a state formed solely by the proximity to a metal rather than from local bonds, has not been observed unambiguously up to now.

So, in this review, we first discuss the fabrication of the well-defined insulator/metal interface in alkali halide/metal systems. Then, we discuss its electronic structure studied by near edge x-ray absorption fine structure (NEXAFS). A clear evidence for the MIGS is observed, and the character of MIGS is discussed [19–21]. Finally, we discuss a possibility of the interface superconductivity.

II. SYSTEM AND EXPERIMENTAL METHOD TO STUDY MIGS

In order to fabricate the well-defined insulator/metal interface, we pay attention to the alkali halides as insulator, according to the following reasons. First, the diversity of lattice constant of alkali halide (from 0.40 nm (LiF) to 0.73 nm (RbI) ) is advantageous for the heteroepitaxial growth, since matching of the lattice constant is important for the heteroepitaxial growth. Second, alkali halides can grow on alkali halides in a layer-by-layer fashion even for the lattice misfit as large as 20%, and at low substrate temperatures [3]. This growth mode is based on the weak bonding of alkali halide molecules to alkali halide surfaces. Alkali halide molecules can easily diffuse to the step edge, enabling the step-flow growth.

By using MBE technique and choosing appropriate combination of alkali halides and metals, we have revealed that single crystalline alkali halide films can grow heteroepitaxially on metal substrates in a layer-by-layer fashion [22–24]. So, the atomically well-defined insulator/metal interfaces can be prepared. In atomic structures of the heterointerface, two types of orientations are found to occur. In the following, we explain the heteroepitaxial growth of alkali halides on metal substrates mainly for LiCl/Cu(001) and LiCl/Ag(001).

Figure 3 (a) shows the typical reflection high energy electron diffraction (RHEED) patterns during the growth of LiCl on Cu and Ag(001) at substrate temperatures of 300 K [22]. In both cases, single crystalline LiCl films grow heteroepitaxially on metal substrates. The streaks in RHEED patterns show that the flatness of the film surface is always maintained during growth, and layer-by-layer growth occurs in both cases. On the other hand, the interface structure is different from each other. For LiCl/Cu(001), LiCl grows with its [100] axis rotated by 45° from that of the Cu(001) substrate ([100]Cu//[110]Cu), while it grows without azimuthal rotation ([100]LiCl//[100]Cu) for LiCl/Ag(001) (see Fig. 3 (b)). In case of LiCl/Cu(001), the interatomic distance of Li-Cl is 0.257 nm and it is close to the Cu-Cu distance. The density functional calculation results show that the LiCl island adsorb on the fourfold hollow site of the first Cu layer [22] and, thus, LiCl the island grows with its [100] axis rotated by 45° from that of the Cu substrate.

In case of LiCl/Ag(001), the difference in the interatomic distance or lattice constant between LiCl and Ag is large, and thus, the commensurate structures can not
be formed at the interface, in which all cations and anions occupy symmetrical sites. The reason why a single crystalline LiCl film can grow heteroepitaxially on Ag(001) without azimuthal rotation is ascribed to the following growth mechanism based on the weak interaction between LiCl and Ag. First, although various steps might exist on a (001) face of an fcc crystal, every step can be thought to consist of two types of steps. Here we define "(110) step", as one which orients in the [110] direction, and "(100) step" as one which orients in the [100] direction. (see Fig. 4 (a)) The (110) step exposes a (111) face, while the (100) step does a (110) face. Since the (111) face is energetically more stable than the (100) face for fcc transition metals, majority of steps on (001) surfaces of fcc transition metals are likely to be (110) steps. Second, conduction electrons do not follow entirely the short-range corrugation of the surface at the steps, and thus, the upper (lower) side of the step edge is positively (negatively) charged (Smoluchowski effect), as shown in Fig. 4 (b) [25]. When alkali halide molecules diffuse to the step sites, cations of alkali halide molecule adsorb preferentially at the negative lower side of the step edge, while anions adsorb preferentially at the positive upper side of the step edge. Therefore, cations (anions) align along the lower (upper) side of the (110) step, as shown in Fig. 4 (c). At the initial stage of the growth, alkali halide molecules are expected to adsorb following this rule. When the succeeding molecule comes to the initially adsorbed molecules, the rocksalt lattice is formed with its [100] axis parallel to the [100] axis of the substrate.

Now, we can prepare the well-defined insulator/metal interface, the way to detect the electronic structure characteristic of the interface is important. In conventional photoemission spectroscopy, a signal from the interface is obscured by that from the substrate. In the previous study, we employed ultraviolet photoemission spectroscopy and EELS to probe the LiCl/Cu(001) interface, but could not find any indication for states characteristic of the interface [26]. So, we adopt species-selective method, Cl-K edge NEXAFS. Cl-K edge NEXAFS is based on the x-ray absorption of the Cl atom [27], and hence provides information on the electronic structure of the alkali halide film (NaCl, LiCl) itself with influences of the substrate negligible. Furthermore, NEXAFS can probe even a deep interface, because the probing depth of NEXAFS with its high-energy photons (∼3000 eV) is 1000nm. It suites for obtaining the dependence of the interface states on the insulating layer thickness. Therefore, NEXAFS is one of the most appropriate methods to study the electronic structure at the insulator/metal interface.

III. EXPERIMENTAL

The experiments were performed in a custom-designed ultrahigh-vacuum (UHV) system with a base pressure of $1 \times 10^{-7}$ Pa. Mechanically and electrochemically polished Cu and Ag(001) crystals were cleaned by repeated cycles of Ar⁺ sputtering and annealing. The sample temperature was monitored with a chromel-alumel thermocouple, which was spot-welded on a Ta sheet attached to the sample surface. After repeated preparation cycles, a sharp
FIG. 4: (a) Schematic top view of steps on (001) surfaces of fcc transition metals; (110) step which orients in the [110] direction, and (100) step which orients in the [100] direction. (b) Basic model of the binding geometry. Because of the Smoluchowski smoothing effect, upper (lower) side of step edges is positively (negatively) charged. Cations adsorb at the lower side of step edges. (c) Sphere model of the alkali halide film grown on (001) face of the fcc transition metal. Cations align along the lower side of the (110) step.

RHEED pattern was observed, and no contaminant was detected by Auger electron spectroscopy (AES). LiCl and KCl were evaporated from Knudsen cells. The growth rate was monitored using a quartz crystal oscillator and it was on the order of 1 mono layer (ML: \( \sim 0.3 \) nm) /min. Real-time observation of crystallinity and orientation of films was done by RHEED.

Cl-K edge NEXAFS measurements were carried out at the soft x-ray double-crystal monochromator station BL-11B of the Photon Factory in High Energy Accelerator Research Organization [28]. 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 [29]. 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.

IV. OBSERVATION OF MIGS

Figure 5 shows the Cl-K edge NEXAFS spectra for LiCl/Cu(001) and LiCl/Ag(001) taken at grazing x-ray incidence for various thicknesses of the LiCl layer. All the spectra are normalized by their edge-jump. As the thickness of the LiCl layer is decreased, a pronounced pre-peak \((p)\) emerges below the bulk edge onset. Since NEXAFS qualitatively provides information on the density of states of unoccupied states, the appearance of the pre-peak below the edge indicates formation of new electronic states below the vacuum level and above the Fermi level in the LiCl films.

There are two points to note about the pre-peak. First, the pre-peak is observed even for the 10 ML LiCl on metal substrates. Since the electronic structure of a free-standing 1 ML film is different from that of a bulk crystal, a new electronic state can be formed apart from bulk band for the free-standing 1 ML film. Therefore, we can not find whether a state observed for a 1 ML film/metal system is characteristic of the interface or one is specific to 1 ML. The fact that the pre-peak is observed even for the thick film shows that the new state is characteristic of the interface. Second, the pre-peak is observed for both LiCl/Cu(001) and LiCl/Ag(001). Although the interface structure is different between LiCl/Cu(001) and LiCl/Ag(001) as discussed in the previous section, the pre-peak is observed in both systems. This indicates that the pre-peak does not originate from local structures at the interface.

To confirm whether the nature of chemical bonds is modified around the interface, we investigated the electronic structure of the LiCl film and the metal substrate with XPS and AES. Figure 6 shows the Cl 1s XPS in LiCl/Cu(001) for various LiCl thicknesses. For comparison, the spectrum and the peak position of bulk LiCl and CuCl are also measured and indicated in the figure. The Cl 1s binding energy of CuCl is lower by 2 eV than that of LiCl. If LiCl interacted with Cu to form a new chemical bond \((i.e., \text{Cl-Cu bond})\) at the interface, a satellite peak at the lower binding energy side or the broadening of the peak would occur. However, the binding energy and the half width of the Cl 1s peak do not change with film thickness, nor does a satellite peak appear in LiCl/Cu(001), indicating that the chemical state of Cl in LiCl/Cu(001) is the same as that of bulk LiCl, with no chemical bonds formed at the interface. Additional point to be noted relates with the position of the Fermi level, which can be estimated from the binding energy of Cl 1s XPS. As indicated in Fig. 5, the Fermi level is located right in the pre-peak and the finite density of states at \(E_F\) implies that LiCl is metallized at the interface.

The chemical state can be investigated by AES [30,
FIG. 5: The Cl-K edge NEXAFS spectra in LiCl films grown on Cu(001) and Ag(001) for various thicknesses of the LiCl layer. All the spectra are normalized by their edge-jump,  $E_F$ indicates the position of the Fermi level as determined from XPS. The x-ray incidence angle is 15°.

FIG. 6: The Cl 1s XPS spectra in LiCl/Cu(001) for various thicknesses of the LiCl 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.

31]. Figure 7 shows the thickness dependence of AES for LiCl/Cu(001). The Cu MMM AES peak, which is surface sensitive, does not shift from that of clean Cu(001) within 0.1 eV, indicating that the interfacial Cu atoms remain almost neutral. These results show that any chemical bond is not formed at the interface.

Here we summarize the above NEXAFS, XPS, and AES results. (NEXAFS) The pre-peak is observed irrespective of the interface structure. (XPS) The chemical state of Cl in LiCl/Cu(001) is the same as that of bulk LiCl. (AES) The interfacial Cu atoms remain almost neutral for LiCl/Cu(001). These results clearly show that the pre-peak observed by NEXAFS originates not from local chemical bonds at the LiCl/metal interface, but from the states formed by proximity to a metal. On the other hand, metal induced gap states originates from the metal wave function penetrating into an insulating side at the insulator/metal interface without forming a chemical bond. Therefore, the pre-peak can be assigned to MIGS. We have obtained unambiguous experimental evidence that MIGS are formed at atomically well-defined alkali halide/metal interfaces by using NEXAFS.
We have then performed a first-principles calculation based on the local density functional theory with pseudopotentials and plane-wave basis to explore how the above experimental result, especially on the MIGS, will fit to the theoretical picture [20]. In the right bottom of Figure 8, we show the slab model of LiCl/Cu(001) with five Cu layers sandwiched from top and bottom by one LiCl layer each. The in-plane unit cell structure contains two Cu atoms and one LiCl. The commensurate structure of the LiCl/Cu(001) interface enables us to adopt this small unit cell. The calculations are performed on periodically repeated slabs, and the slabs are separated by a vacuum of height 5nm.

Figure 8 shows the band structure of 1 ML LiCl/Cu(001) and a free-standing 1 ML LiCl film. For the latter a clear band gap can be seen, although the size of the gap is, as usually the case with LDFT, underestimated by 2-3 eV. When the 1 ML LiCl is put on Cu(001), new bands appear in the gap. We have then characterized their nature by looking at the amplitude of the LDA wave functions. In the green square below the band structure, the contours of the absolute value of the LDA wave functions for the in-gap states are shown. If we look at the three states just above E_F at Γ point, the two closest to E_F right in the bad gap region (red) have indeed amplitudes that are localized to the Cl and Cu atoms at the interface. Existence of such a state is rather surprising, given the fact that LiCl is a good insulator. We can identify that the MIGS observed by NEXAFS should correspond to these states just above E_F. Seen from the contours of the absolute value of the LDA wave functions, the states are revealed to have a p_z-like structure, which is consistent with the result of the polarization dependence of NEXAFS, as discussed in the following.

We have substituted the Cu substrate with a jellium to examine whether a simplest possible model for the electron gas would exhibit MIGS. The new in-gap states whose amplitude of the LDA wave functions reside on the Cl atoms at the interface, appears for LiCl/jellium system. The appearance of MIGS for LiCl on jellium endorses that MIGS is characteristic of insulator/metal interfaces rather than from local modifications in the chemical bonds.

V. CHARACTER OF MIGS

As we have shown experimental and theoretical evidences for the formation of MIGS at alkali halide/metal interfaces, so let us discuss the character of the MIGS in more detail. First, anisotropy of MIGS is studied by polarization dependent NEXAFS. Figure 9 shows the polarization dependence of NEXAFS for LiCl/Cu(001) and LiCl/Ag(001). The x-ray incidence angle is 15, 55 and 90°. Intensity of the pre-peak is greater for grazing x-ray incidence (15°) than normal incidence (90°). The inten-
sity of the NEXAFS peak is proportional to \( \cos^2 \theta \), where \( \theta \) is the angle between the electric vector of the x-ray and the transition moment of the excitation [27]. The electronic state whose wave function orients in the surface parallel (normal) direction is selectively detected for grazing (normal) x-ray incidence. Therefore, the observed polarization dependence results indicate that the MIGS have a \( p_x \) (\( z \perp \) surface) like character, which is consistent with the above DFT calculation results.

Second, the spatial distribution of MIGS in the surface normal direction is discussed in terms of decay length. The decay length is estimated according to the following procedure. First, the pre-peak of the film is extracted by subtracting the bulk component. Figure 10 shows the thickness dependence of the intensity of the pre-peak (not normalized by edge-jump) for LiCl/Cu(001), Ag(001), together with that for KCl/Cu(001) and KCl/Ag(001).

VI. POSSIBILITY OF SUPER CONDUCTIVITY AT THE INSULATOR/METAL INTERFACE

Finally, let us point out that the electronic structure specific to the insulator/metal interface can possibly have interesting implications for superconductivity. Discussions on superconductivity at interfaces have a long history. A well-known proposal is the superconductivity by exciton mechanism at metal/semiconductor interfaces [33]. The presence of excitons require a wide-gap semiconductor. However, this will prevent the metallic carriers to penetrate into the semiconductor, and thus, the coexistence (in real space) of excitons and metallic carriers are
FIG. 11: The schematic view of a hypothetical semiconductor with both a small band gap and a wide band gap.

difficult. To circumvent this, they have considered a hypothetical semiconductor with a specific density of states that has two closely separated peaks in a wide band gap as shown in Fig. 11. Namely, the large band gap is required for excitons to be formed, while two narrow-gap peaks are required to enable the carriers in the metallic side to easily tunnel into the semiconductor side.

By sharp contrast, the insulator/metal interface with the MIGS makes it possible to coexist excitations (associated with a wide band gap (∼9 eV)) and carriers (MIGS) without introducing fictitious density of states. To have a high $T_c$, the carriers and the excitons have to interact strongly. This condition can be satisfied at the insulator/metal interface because of the penetration of MIGS into the insulating layer. So we may expect that the insulator/metal interface such as those discussed here may provide a possible ground for superconductivity.

VII. CONCLUSIONS

We have obtained unambiguous experimental evidence that MIGS are formed at atomically well-defined alkali halide/metal interfaces by using NEXAFS. Experimental results with XPS, AES, and theoretical result with LDA all indicate that the MIGS originate from the proximity to a metal rather than from local modification of the chemical bonds. The spatial distribution of MIGS is studied by the polarization and thickness dependent NEXAFS. The polarization dependence clearly shows that the MIGS have a $p_z$ ($\perp$ surface) like character. The decay length of MIGS depends on rather an alkali halide than a metal, and it is larger for alkali halides with smaller band gap energy. We also discuss a possibility of the interface superconductivity.

Acknowledgments

The authors would like to thank the following persons for collaborations of the present work: Professor H. Aoki, Dr. R. Arita, Dr. G. Yoshikawa, Dr. S. Ikeda, Dr. M. Katayama, Mr. S. Entani, H. Inoue and Professor A. Koma. This work was supported by a Grant-in-Aid for Scientific Research and Special Coordination Fund from the Ministry of Education of Japan. (Creative Scientific Research Project, No.14GS0207). The present work was performed under the approval of Photon Factory Program Advisory Committee (PF-PAC No.2001G336).

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