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Two types of epitaxial orientations for the growth of alkali halide on fcc metal substrates

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Thin-film growth of alkali halides on (001) surfaces of fcc transition metals was studied using reflection high-energy electron diffraction. Alkali halide grew with its [100] axis rotated by 45° from that of the metal substrate ($[100]_{film}//[110]_{substrate}$) for LiCl/Cu(001) and LiCl/Ni(001). On the contrary, alkali halide grew without azimuthal rotation ($[100]_{film}//[100]_{substrate}$) for LiCl/Ag(001), NaCl/Cu(001), NaCl/Ag(001), and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$. The former growth mode ($[100]_{film}//[110]_{substrate}$) occurred only with a small difference in the first-nearest neighbor (first-NN) interatomic distance between alkali halide and metal. The latter growth mode ($[100]_{film}//[100]_{substrate}$) occurred even with a large difference in the first-NN interatomic distance. The mechanism of the latter growth was explained by the preferential direction of steps on (001) surfaces of fcc metals and the migration of alkali halide molecules to the steps.

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I. INTRODUCTION

Recent development of molecular-beam epitaxy (MBE) technique has made it possible to produce various types of heterostructures, which not only achieve improved semiconductor devices but also present hitherto unknown physical phenomena. Most of the earlier studies on MBE dealt with semiconductors and metals for the purpose of technological application. Recently, however, there has been a growing interest in the MBE of insulating materials on metal substrates due to their importance in catalysis, device applications, and fundamental science. On the technological side, they are of considerable importance as insulating barriers in miniaturized electronic circuits, and as magnetic tunnel junctions for magnetoelectronics and magnetic data storage. On the fundamental side, various properties, such as band-gap narrowing, metal-insulator transition, etc., are expected at the metal-insulator interface from theoretical calculations.[1,2] Furthermore, there is a strong interest in the nature of the solid-solid interface between very dissimilar materials.

An alkali halide is a typical insulator with a wide band gap. From a historical viewpoint, the epitaxy of alkali halides was studied about seventy years ago, and alkali halides were the top runners in the field of epitaxial film growth. The epitaxial growth is also observed for metals on alkali halides, such as Ni, Cu, Ag, and Au on NaCl substrate.[3] Compared with the growth of metals on alkali halides, fewer studies were done on the reverse system, that is, the growth of alkali halides on metals. Very recently, thin films of alkali halides grown on single-crystalline metal substrates were studied using low-energy electron diffraction, scanning tunneling microscope (STM), and dynamic force microscope.[4–11] Fölsch *et al.* grew a NaCl film on Cu(211) and revealed that (311) and (100) facets are formed at substrate temperatures higher than 300 K.[4] Hebenstreit *et al.* grew a NaCl film on Al(111) by subsequent adsorption of Na and Cl_2 at 300 K, and succeeded in growing the (111) bulk terminated NaCl island.[5] Farias *et al.* investigated growth of LiF on Ag(111) at a substrate temperature of 77 K, and found that nucleation of LiF molecules begins from step edges.[6] Bennewitz *et al.* found that a NaCl film grows on Cu(111) with the azimuthal orientation (NaCl[100]//Cu[110]), and the NaCl(001) film grows in a carpetlike mode, that is, the film lies like a carpet over steps.[7,8] These works dealt with films thinner than 3 ML, and did not discuss the structures of thin films from the viewpoint of epitaxial growth.

Recently, we have revealed that a single-crystalline LiCl film grew heteroepitaxially on Cu(001).[12] Cu is a typical metal of the fcc structure with a lattice constant of 3.61 Å at 300 K, and the first-nearest neighbor (first-NN) Cu-Cu distance is 2.56 Å. On the contrary, LiCl is a typical insulator of the rocksalt structure with a lattice constant of 5.13 Å at 300 K and the first-NN Li-Cl distance is 2.57 Å. The difference in the first-NN interatomic distance is, thus, only 0.4% for LiCl/Cu(001). At a substrate temperature of 300 K, a single-domain LiCl film ($[100]_{film}//[110]_{substrate}$) grew in a layer-by-layer fashion, while a double-domain LiCl film ($[100]_{film}//[100]_{substrate}$ and $[100]_{film}//[110]_{substrate}$) grew at substrate temperatures higher than 420 K. The density-functional calculation showed that the LiCl island was adsorbed on the fourfold hollow site of the first Cu layer.

For further understanding of the growth of alkali halides on metals, we have studied thin-film growth for various alkali halide(film)–metal(substrate) combinations. The systems investigated here were LiCl/Ni(001), LiCl/Ag(001), NaCl/Ni(001), NaCl/Cu(001), NaCl/Ag(001), and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$, where the difference in the first-NN interatomic distance between alkali halides and metal were 2.9, −11.2, 13.2, 10.3, −2.4, and 0.0 %, respectively. Two types of epitaxial orientations were observed for the growth of alkali halides on metals. The epitaxial orientation was explained by the difference in the first-NN interatomic distance and surface diffusion of alkali halide molecules on metals.

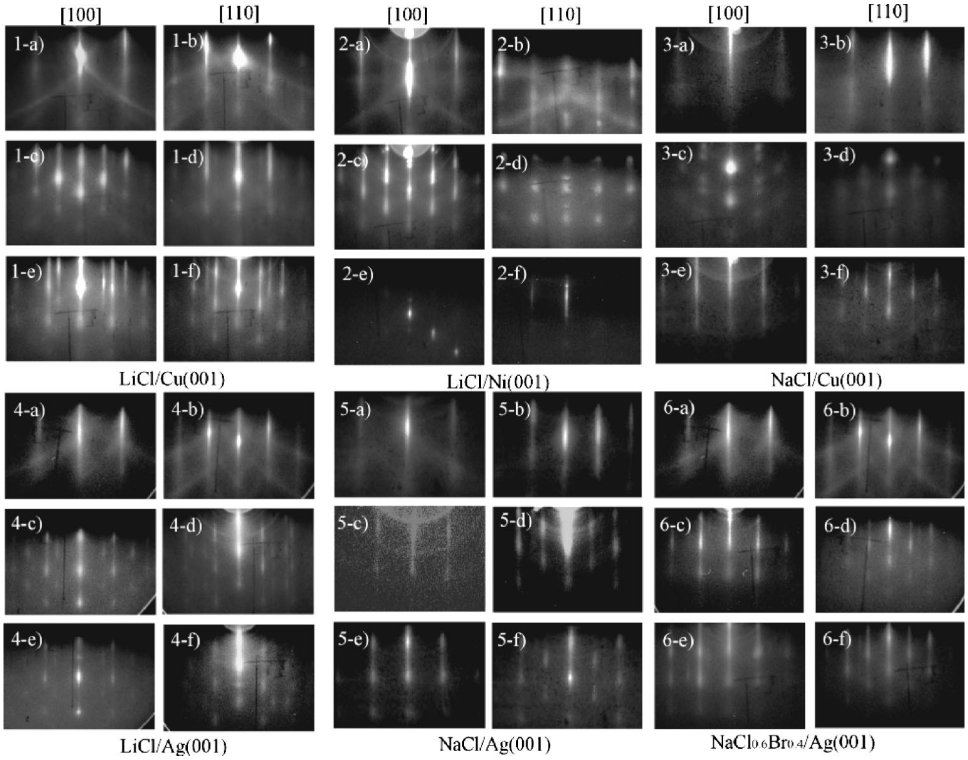


FIG. 1. A typical sequence of RHEED patterns during growth of alkali halides on metal substrates. (1) LiCl/Cu(001), (2) LiCl/Ni(001), (3) NaCl/Cu(001), (4) LiCl/Ag(001), (5) NaCl/Ag(001), (6) $NaCl_{0.6}Br_{0.4}$/Ag(001). (a), (b) 0 ML (metal substrate), (c), (d) 20 ML at 300 K, (e), (f) 20 ML at 420 K. The incident beam was parallel to the [100] (a), (c), (e) or [110] (b), (d), (f) azimuth of the substrate.

II. EXPERIMENTS

The experiments were performed in a custom-designed ultrahigh-vacuum system with a base pressure of 1×10^{-7} Pa. Mechanically and electrochemically polished Cu, Ag, and Ni(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 reflection high-energy electron diffraction (RHEED) pattern was observed, and no contaminant was detected by Auger electron spectroscopy (AES). A solid solution $NaCl_{0.6}Br_{0.4}$ was prepared by mixing appropriate amounts of NaCl and NaBr, followed by repeated treatments of grinding and melting. LiCl, NaCl, and $NaCl_{0.6}Br_{0.4}$ were evaporated from Knudsen cells. The growth rate was monitored using a quartz crystal oscillator and it was on the order of 1 ML (2.6 Å) /min. Real-time observation of crystallinity and orientation of films was done by RHEED. Surface atomic compositions of the deposited films were investigated *in situ* by AES.

III. RESULTS

Figure 1 shows typical RHEED patterns during the growth of alkali halides on metal substrates at substrate temperatures of 300 K and 420 K. The incident electron beam was parallel to the [100] or [110] azimuth of the substrates. We could grow single-crystalline alkali halide films heteroepitaxially on metal substrates for some alkali halide–metal combinations. Figure 2 summarizes the orientations of the alkali halide film on metal substrates. Two types of orientations were found to occur for the heteroepitaxial growth of alkali halides on metals. One corresponds to the growth with its [100] axis rotated by 45° from that of the metal substrate ($[100]_{film}//[110]_{substrate}$) and another without azimuthal rotation ($[100]_{film}//[100]_{substrate}$). Hereafter, these growths are denoted as the 45° growth and the 0° growth, respectively. The 45° growth appeared for LiCl/Cu(001) [see Fig. 1(1)] and LiCl/Ni(001) [see Fig. 1(2)], where the difference in the first-NN interatomic distance was small. The 0° growth appeared for NaCl/Cu(001) [see Fig. 1(3)] and LiCl/Ag(001) [see Fig. 1(4)], where the difference in the first-NN interatomic distance was not small. The 0°

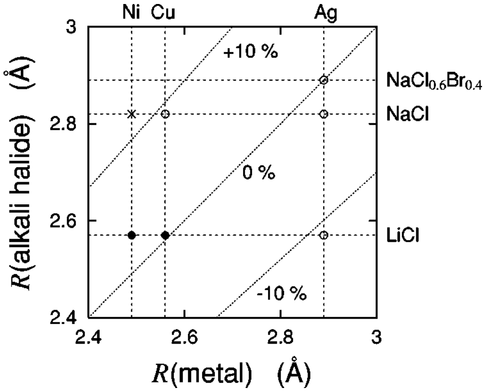


FIG. 2. Relation between the growth mode and the difference in the first-NN interatomic distance (R) for various alkali halide–metal systems. Filled circles, circles, and crosses denote the epitaxial growth with the [100] axis of the alkali halide rotated by 45° from that of the metal substrate (45° growth), the epitaxial growth without azimuthal rotation (0° growth), and the nonepitaxial growth, respectively. For LiCl/Cu(001), both the 0° growth and the 45° growth occurred at 420 K. For NaCl/Cu(001), epitaxial growth did not occur at 300 K.

growth also occurred for NaCl/Ag(001) [see Fig. 1(5)], where the difference in the first-NN interatomic distance was small. Since streaks were sharper for 420 K than for 300 K in case of NaCl/Ag(001) and LiCl/Ni(001), the crystallinity of grown films increased with substrate temperature. A polycrystalline film grew at 300 K for NaCl/Cu(001), and epitaxial growth did not occur at all for NaCl/Ni(001). For LiCl/Ag(001), part of LiCl islands grew with their [100] axis rotated by 45° from that of the Ag substrate, though most of LiCl islands grew without azimuthal rotation.

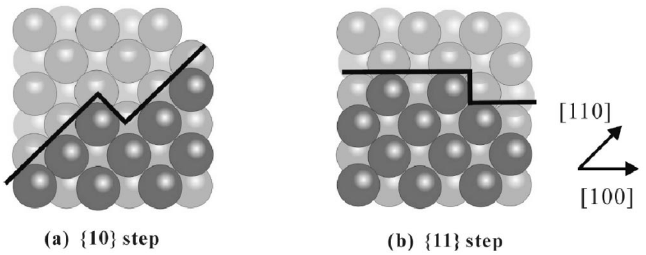
Since the difference in the first-NN interatomic distance between NaCl and Ag was only −2.4%, the 45° growth was expected to occur for NaCl/Ag(001), as is the case with LiCl/Cu(001). However, the 0° growth occurred for NaCl/Ag(001). This epitaxial orientation seems strange, because the difference of interatomic distance in the [100] or [110] azimuth of the substrate is larger for this orientation (−31%) than for the 45° rotation (−2.4%). In order to clarify the relation between the difference in the first-NN interatomic distance and the epitaxial orientation, we have studied the growth of alkali halides corresponding to the complete matching of the first-NN interatomic distance. This was realized by forming an alkali halide solid solution. In general, a solid solution is a material, which is composed of a mixture of atoms or molecules over a wide range of compositions, and still remains a single phase. The lattice constants of the grown films can be controlled by changing the mixing ratio.[13] The lattice constant of $\mathrm{NaCl_{0.6}Br_{0.4}}$ is 5.78 Å and the average first-NN interatomic distance is 2.89 Å, which is equal to the Ag–Ag distance. Figure 1(6) shows that the 0° growth occurred for $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$ at 300 K and 420 K, as is the case with NaCl/Ag(001). These results showed that the difference in the first-NN interatomic distance did not necessarily determine the epitaxial orientation, at least for the growth on Ag substrates. The sharp streaks at 420 K indicate that the grown film was flat and the layer growth occurred.

IV. DISCUSSION

A. Growth of alkali halides on various substrates

It is well known that the lattice matching condition plays a decisive role in the film growth. Severe lattice matching conditions are required for the heteroepitaxial growth of semiconductor and oxide with anisotropic covalent bonds.[14,15] This growth mode is based on the strong covalent bond formed at the interface. However, the lattice matching condition is mild for the heteroepitaxial growth of alkali halides with isotropic ionic bonds. Alkali halides grow in a layer-by-layer fashion even for the lattice misfit as large as 20%. This growth mode is based on the weak bonding of alkali halide molecules to alkali halide (100) surfaces.[16–19]

In addition to the heteroepitaxy among the same material group, we should pay attention to the heteroepitaxy, in which there is a large difference in chemical bonds between films and substrates. For the growth of alkali halides (ionic bond) on semiconductors (covalent bond), epitaxial growth occurs with the severe lattice matching condition.[13,20,21] This means the formation of chemical bond between the dangling bond of a covalent semiconductor and the atom of an ionic compound. In the present study, we have found that some alkali halides grew heteroepitaxially on metal substrates even with a large lattice misfit, difference in the first-NN interatomic distance. These facts suggest the absence of chemical bond at the interface and the weak interaction between metal and alkali halide.



(a) {10} step **(b) {11} step**

FIG. 3. Schematic top view of steps on (001) surfaces of fcc transition metals. (a) steps that consist of the {10} step, (b) steps that consist of the {11} step.

The present experimental results showed that both the 45° growth and the 0° growth could occur for the growth of alkali halides on metal substrates. The 45° growth occurred only for the small difference in the first-NN interatomic distance such as LiCl/Cu(001) and LiCl/Ni(001). In this case, cations and anions were located at a fourfold hollow site, which was indicated by density-functional calculation for the LiCl/Cu(001).[12] The same interface structure was expected for LiCl/Ni(001). However, the 0° growth occurred even for the systems with a large difference in the first-NN interatomic distance. In this orientation, the commensurate structures, in which all cations and anions occupied such symmetrical sites, as hollow, atop, and bridge site, could not be formed at the interface. It is, thus, difficult to explain the 0° growth from the viewpoint of the stability of the local structure. Furthermore, the 0° growth occurred for NaCl/Ag(001) and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$, in which the difference in the first-NN interatomic distance was small. Therefore, two subjects should be solved to explain the growth of alkali halides on metals. One is the mechanism of the 0° growth. Another is the reason why the 0° growth occurred for NaCl/Ag(001) and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$, where the difference in the first-NN interatomic distance was small.

B. Mechanism of the 0° growth

First, the mechanism of the 0° growth would be discussed. It is well known that the step-flow growth occurs for alkali halides on alkali halides.[16–19] This growth is ascribed both to the weak bonding of molecules to a terrace, and to the strong bonding to a step edge. The chemical interaction between metals and alkali halides is also weak, as discussed in the preceding subsection. Therefore, steps are expected to play a decisive role in the film growth of alkali halides on metals, because of the weak bonding of alkali halide molecules to metal substrates. Recent STM works have revealed that nucleation of alkali halide molecules begins at step edges.[5,6] Therefore, it is necessary to consider the preferen-

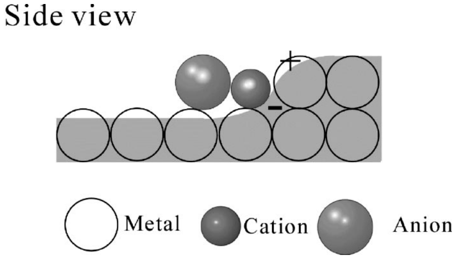


FIG. 4. Basic model of the binding geometry. Because of the Smoluchowski smoothing effect, upper (lower) side of step edges is positively (negatively) charged. Cations adsorb at the lower side of step edges.

tial direction of steps on (001) surfaces of fcc transition metals, and the role of the step in the growth of alkali halides on metals.

Although various steps might exist on a (001) face of fcc crystal, every step can be thought to consist of either the {10} step or the {11} step, as shown in Fig. 3. The {10} step exposes a (111) face, while the {11} step exposes a (100) 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 the {10} steps. Vitos *et al.* calculated the formation energy of steps on surfaces of bcc and fcc transition metals.[22] The {10} step is more stable than the {11} step by a factor of two for (001) surfaces of fcc transition metals. Alverz *et al.* studied homoepitaxial growth of Ag(001) by x-ray diffraction.[23] The {10} island edge can be considered to be preferred to the {11} island edge, since Ag island grows with its dendritic arms along the {10} directions. All these facts indicate that the preferential direction of step is parallel to the {10}.

According to Smoluchowski, two effects are responsible for the charge distribution at a metal surface.[24] The first effect is the relatively slow drop of electron density perpendicular to the surface. The second effect, the so-called smoothing, implies that conduction electrons do not follow entirely the short-range corrugation of the surface. While Smoluchowski discussed the influence of surface corrugation on the work function, we will now focus on the charge distribution at step edges. Because of the Smoluchowski effect, the upper (lower) side of the step edge is expected to be positively (negatively) charged, as shown in Fig. 4.[25] One can expect that cations of alkali halide molecules adsorb preferentially at the negative lower side of the step edge, while anions adsorb preferentially at the positive upper side of the step edge. This heterogeneous nucleation induced by step dipoles was also discussed to explain the growth behavior of LiF on Ag(111).[6] Since most of steps on (001) surfaces of fcc transition metals are the {10} steps, cations (anions) align along the lower (upper) side of the {10} step. At the initial stage of the growth, alkali halide molecules might adsorb under this condition. When the succeeding molecule comes to the initially adsorbed molecules, the rocksalt lattice can be formed with its [100] axis parallel to the [100] axis of the substrate, as shown in Fig. 5. This might be possible because of the weak interaction of alkali halide molecules with the metal surface. The mechanism of the 0° growth in Fig. 5 could be explained by the preferential direction of steps on (001) surfaces of fcc metals and the Smoluchowski effect.

C. The 0° growth for a small difference in interatomic distance

The above discussion shows that the 0° growth occurs, when alkali halide molecules diffuse to step edges and the heterogeneous nucleation occurs at steps. In this subsection, we will discuss the decisive factor of the epitaxial orienta-

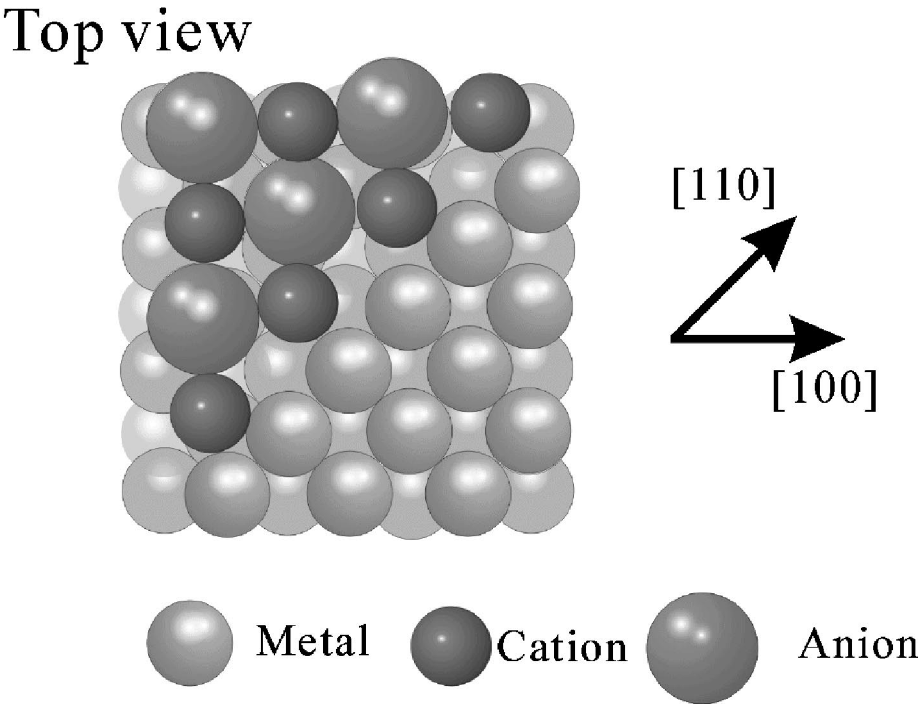


FIG. 5. Sphere model of the alkali halide grown on (001) face of fcc transition metal. Cations align along the lower side of the {10} step, because of the Smoluchowski smoothing effect.

tion. In the case of 0° growth, the surface diffusion constant (D_s) is important to discuss the growth of alkali halides on metals. However, D_s has not been studied for alkali halide molecules on metal substrates as far as we know. Therefore, we will discuss a binding energy (E_b) instead of D_s according to the following reason. First, D_s decreases with increase in the activation energy of surface diffusion (E_{ds}), because D_s is given by $D_s = a^2 \nu \exp(-E_{sd}/kT)$, where a and ν are the lattice constant and the frequency of the adsorbate, respectively. Second, although E_b does not directly relate to E_{ds}, theoretical calculations have revealed that E_{ds} is about 30% of E_b for the metal atoms on alkali halide substrates, and they can be considered to correlate strongly with each other.[26] Therefore, it can be said that D_s decreases with increase in E_b.

Next, E_b of Ni, Cu, and Ag would be discussed by considering experimental and theoretical calculation results. First, the heat of adsorption can be used as a measure of E_b, and it decreases monotonically as one proceeds from left to right across any transition-metal row in the periodic table. For example, the heat of absorption of CO on Ni is about twice as large as that on Cu and Ag.[27] Second, the Cl-metal distance is 2.35 Å for Cl/Ni(001), 2.40 Å for Cl/Cu(001), and 2.61 Å for Cl/Ag(001). Finally, E_b of an alkali halide to a metal substrate was 0.80 eV/molecule for LiCl/Cu(001) and 0.60 eV/molecule for NaCl/Ag(001), determined by the density-functional calculation.[28] These facts indicate that E_b of gas, molecules, and alkali halide molecules to Ni, Cu, and Ag surfaces decreases in that order. Consequently, D_s is the largest for Ag.

Finally, we will estimate E_{ds} using the above data. E_{ds} of alkali halide molecules on alkali halide substrates is $\leqslant$0.2 eV/molecule,[18,19] where the step-flow growth occurs at 130–500 K. For LiCl/Cu(001) and NaCl/Ag(001), E_{ds} was calculated to be 0.2 eV/molecule, assuming that it was 30% of E_b. This small E_{ds} (especially on Ag) is comparable to E_{ds} of alkali halide molecules on alkali halide substrates, and small enough for alkali halide molecules to diffuse to step edges. Consequently, the heterogeneous nucleation occurred at steps, and the 0° growth was achieved for NaCl/Ag(001) and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$, though the difference in the first-NN interatomic distance was small.

D. Decisive factor of the epitaxial orientation

From the above discussion, the experimental results could be explained qualitatively in terms of D_s and difference in the first-NN interatomic distance. First, we would consider the system, where the difference in the first-NN interatomic distance is small. For LiCl/Ni(001), because of small D_s and large E_b, LiCl molecules adsorbed strongly at the hollow site and did not diffuse to step edges. The 45° growth, thus, occurred for LiCl/Ni(001). For NaCl/Ag(001) and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$, the 0° growth occurred because of large D_s, as discussed in the preceding subsection. For LiCl/Cu(001), alkali halide molecules interacted moderately with the Cu substrate. Due to the small D_s, alkali halide molecules could not diffuse to step edges at 300 K, and they adsorbed at the hollow site. At elevated substrate temperature (420 K), D_s increased and the number of molecules, which could diffuse to step edges, increased. Therefore, both the 0° growth and the 45° growth occurred simultaneously at 420 K. Second, we would discuss the system of the large difference in the first-NN interatomic distance. For LiCl/Ag(001), the heterogeneous nucleation at steps (the 0° growth) occurred because of large D_s. For NaCl/Ni(001), however, alkali halide molecules could not diffuse to step edges because of the small D_s. Since the large difference in the first-NN interatomic distance prevented the commensurate growth, a single-crystalline NaCl film did not grow on Ni(001) at 300 K and 420 K. For NaCl/Cu(001), however, alkali halide molecules interacted moderately with the Cu substrate. Although a single domain NaCl film did not grow on Cu(001) because of small D_s at 300 K, the heterogeneous nucleation at steps (the 0° growth) occurred when D_s was increased at 420 K.

E. Application

One of the prominent features of alkali halide growth is that alkali halides can grow on alkali halides in a layer-by-layer fashion even for the lattice misfit as large as 20%.[16–19] Alkali halides are, thus, often used as a buffer layer to connect dissimilar materials. For example, single-crystalline MgO, NiO, and CoO thin films can be grown heteroepitaxially on GaAs(100) by using NaCl and LiF buffer layers.[29,30] In the present study, single-crystalline alkali halide films could grow heteroepitaxially on metal substrates. Therefore, we could present a different method to grow single-crystalline thin films of various materials, such as ferromagnetic oxides, on metal substrates.

On the fundamental side, the ideal insulator-metal interface was realized for the present alkali halide–metal systems. It is true that some oxides grow heteroepitaxially on metal substrates, and electronic structures of the systems have been studied as a model system of metal-insulator interface. However, metal substrates might be oxidized, since oxides were grown by evaporating metal in an oxygen atmosphere. Therefore, the oxide-metal system is not appropriate for studying the electronic structure of the insulator-metal interface. However, the metal substrate does not oxidize for alkali halide–metal systems. Using this ideal insulator(alkali halide)-metal interface, we can study the electronic structure of the insulator-metal interface, such as band gap, charge transfer energy, and Coulomb interaction.

V. CONCLUSIONS

Thin-film growth of alkali halides on (001) surfaces of fcc transition metals was studied using RHEED. Some alkali halides could grow heteroepitaxially on metal substrates even with a large difference in the first-NN interatomic distance. Alkali halide grew with its [100] axis rotated by 45° from that of the metal substrate ($[100]_{film}//[110]_{substrate}$) for LiCl/Cu(001) and LiCl/Ni(001), while alkali halide grew without azimuthal rotation ($[100]_{film}//[100]_{substrate}$) for LiCl/Ag(001), NaCl/Cu(001), NaCl/Ag(001), and $\mathrm{NaCl_{0.6}Br_{0.4}/Ag(001)}$. The growth mode and epitaxial orientation were explained by the difference in the first-NN interatomic distance and the binding energy between alkali halides and metals. The 45° growth occurred, when the difference in the first-NN interatomic distance was small and the bonding of alkali halide to metal was strong. When the bonding of alkali halide to metal was weak, heterogeneous nucleation occurred at steps, in which the 0° growth was realized. In the case of the 0° growth, the crystallinity was improved for increasing the substrate temperature.

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