Alkali-Metals on ZnO(10\(\overline{1}0\)) Studied by Low-Energy Electron Diffraction and Photoelectron Spectroscopy*

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The geometric and electronic properties of alkali metals (Na and Cs) on ZnO(10\(\overline{1}0\)) are investigated by means of photoelectron spectroscopy and low energy electron diffraction (LEED). Growth of the Na overlayer on ZnO(10\(\overline{1}0\)) at room temperature is characterized by layer-by-layer growth or monolayer growth followed by three-dimensional cluster growth. The Na adatoms in the first layer are in a cationic state, and the metallic phase is formed on top of the first cationic layer. Although Na deposition at room temperature does not yield any long-range ordered superstructure, annealing the Na-covered surface results in a (1\(\times\)3) LEED pattern, and we propose the formation of the Na atomic chains along the Zn–O dimer rows. For the Cs adsorption system, the disordered overlayer by ionized Cs adatoms is also formed throughout the submonolayer coverage region. Unlike the Na adsorption system, heat treatment of the Cs-covered surface does not yield any ordered structure until all Cs adatoms desorb from the surface. [DOI: 10.1380/ejssnt.2005.299]

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I. INTRODUCTION

Alkali metals (AM’s) are important additives for heterogeneous catalysis because AM-doped catalysts often exhibit higher reactivity and/or alter selectivity of reaction products that the corresponding undoped catalysts do not possess. For example, the Cu/ZnO catalyst, which is a renowned catalyst for methanol synthesis from syngas [1], gives a higher yield of higher alcohols such as propanol and butanol when the catalyst is doped with the Cs atoms [2, 3]. A similar effect is also found for the K-promoted ZnO catalyst, which is found to be efficient for isobutanol synthesis, in sharp contrast to the undoped ZnO catalyst, which does not yield isobutanol [4, 5]. A precise role of doped AM’s in these catalytic reactions has not been fully understood. Thus, it is important to study the adsorption state of AM’s and their behavior on the ZnO surface, especially at working temperatures between 500 and 700 K [1–5].

ZnO crystallizes into the wurtzite structure, and the electrically polar Zn-terminated (000\(\overline{1}\)) and O-terminated (000\(\overline{1}\)) surfaces and the nonpolar (10\(\overline{1}\)0) surface have been the objects of extensive experimental and theoretical studies. However, an understanding of the AM interaction with the low-index surfaces of ZnO has been limited so far. Leysen et al. [6] and Purdie et al. [7] have examined the adsorption state of K and Cs on the ZnO(000\(\overline{1}\)) surface and have found that the (\(\sqrt{3}\)\(\times\)\(\sqrt{3}\))R30\(^{\circ}\) and p(2\(\times\)2) superstructures are formed when K- and Cs-covered surfaces are annealed at moderate temperatures (600–900 K). Madelung potential calculations have indicated that the Cs adatoms in the (\(\sqrt{3}\)\(\times\)\(\sqrt{3}\))R30\(^{\circ}\) phase are partially ionized in order to stabilize the electrically polarized surface [6]. Structural analysis of the adsorbed K atoms in a p(2\(\times\)2) overlayer has supported such an electrostatic consideration [7]. In our previous photoelectron spectroscopy (PES) study for the K/ZnO(10\(\overline{1}0\)) system [8], we have proved from the work function change, K-induced bending of the substrate’s band and the lineshape of the K 2p PES peak that adsorbed K is in an ionic state up to the saturation coverage. We have also found that, as the K-covered ZnO(10\(\overline{1}0\)) surface is annealed, c(2\(\times\)2) and (1\(\times\)3) low energy electron diffraction (LEED) patterns appear at annealing temperatures of 1000 and 1100 K, respectively [8]. We have concluded that these patterns should originate from the ordered structure by the K adatoms, although some contribution of the accumulated O atoms on the surface region, which migrate from the bulk inside upon annealing, is expected [9].

In the present work, we have extended our study to AM’s other than K, i.e., Na and Cs, and have examined the adsorption process, the adsorption state as well as the structure by the AM adatoms on ZnO(10\(\overline{1}0\)) by PES and LEED. For the Na adsorption system, the Na adatoms are ionized when they are in direct contact with the ZnO(10\(\overline{1}0\)) surface, whereas the metallic phase is developed on top of the first cationic Na overlayer. A cationic adsorption state is also observed for the Cs adsorption state up to the monolayer coverage. Room-temperature adsorption of both Na and Cs does not yield any ordered overlayers, but the (1\(\times\)3) structure is induced for the Na adsorption system when the Na-covered surface is annealed. During heat treatment of the Na- and Cs-covered surfaces, bulk diffusion of the adsorbed AM atoms does
not take place, but the accumulation of the O adatoms on the surface is suggested.

II. EXPERIMENTAL

A ZnO single crystal with the (10\(\bar{1}0\)) orientation (MaTecK) was polished mechanically with diamond paste. The crystal was degreased by ultrasonic cleaning in acetone. The sample was mounted on a Ta holder and inserted into an ultrahigh vacuum (UHV) chamber. The cleaning procedure in the UHV chamber was as follows: Repeated cycles of Ar\(^+\) sputtering (1 kV, 2–5 \(\mu\)A) and annealing at 1000 – 1050 K were carried out. Sample annealing was done by heating the Ta plate, which was in direct contact with the rear of the sample crystal, by electron bombardment. A chromel–alumel thermocouple was used to monitor the temperature of the sample surface. The sputtering/annealing cycles were carried out until impurities such as carbon and Au’s were not detected in X-ray PES (XPS) spectra or the Auger electron spectroscopy (AES) spectra. The sample was then heated to 700 K in O\(_2\) atmosphere (\(\sim 2 \times 10^{-6}\) Torr) for \(\sim\) 10 min and cooled to 500 K before O\(_2\) was pumped out. After cooling to room temperature, the sample was heated to 600 K in UHV. The clean surface thus prepared gave a sharp (1x1) LEED pattern. The work function of the clean surface was typically 4.5–4.9 eV, in good agreement with the literature values of 4.64–5.05 eV [10–12].

Na and Cs were deposited onto the surface at room temperature by resistive heating of the thoroughly degassed dispensers (SAES Getters Japan). The pressure during the deposition increased gradually but kept below \(3 \times 10^{-9}\) Torr.

XPS and LEED measurements for both Na and Cs adsorption systems were performed in the UHV system with the base pressure of 6 \(\times\) \(10^{-10}\) Torr. A Mg/Al dual anode X-ray source (XR3E2, VG Microtech), a home-build He discharge lamp, a hemispherical electron energy analyzer (100AX, VG Microtech) and LEED optics were mounted in the UHV chamber. For the XPS measurements, the unmonochromatized Al K\(_\alpha\) line \((h\nu = 1486.6\) eV) was utilized. The sample was oriented so that the incidence angle of the X-ray beam was 48° from the surface normal direction. The entrance of the electron energy analyzer was placed in the normal direction of the sample surface. In the XPS spectra presented below, the binding energy of photoelectron was calibrated by the position of the Zn 2p\(_{3/2}\) peak of the clean ZnO (10\(\bar{1}0\)) surface at 1022.5 eV [13].

For the Na/ZnO(10\(\bar{1}0\)) system, the valence band spectra were measured utilizing the synchrotron radiation at the beam line 11C of the Photon Factory, High Energy Accelerator Research Organization (KEK). The UHV chamber was equipped with a hemispherical electron energy analyzer (VSW HA54) with a microchannel-plate electron multiplier detector for the angle-resolved PES (ARPES) measurements, a single-pass cylindrical mirror analyzer for the AES measurements and LEED optics. The base pressure of the UHV system was 2 \(\times\) \(10^{-10}\) Torr. The incidence angle of the light was 35° from the surface normal, and the photoelectrons emitted to the normal direction were corrected. The binding energy of the valence band spectra were referenced to zero at the Fermi energy, which was determined from the spectra of the Ta holder.

III. RESULTS AND DISCUSSION

A. Na adsorption process

Figs. 1a and 1b show the change in the Na 1s and Zn 2p\(_{3/2}\) core-level spectra, respectively, as a function of the Na coverage (\(\Theta_{Na}\)). Growth of the Na 1s peak and a gradual attenuation of the Zn 2p\(_{3/2}\) peak are observed. The deposition-time dependence of the Na 1s and Zn 2p\(_{3/2}\) peak intensities is plotted in Fig. 1c. Here, linear growth of the Na 1s peak intensity is seen with a kink at \(\sim 1.5\) min. The Zn 2p\(_{3/2}\) peak, on the other hand, decreases linearly, and a kink also appears at \(\sim 1.5\) min. The observed change in the peak intensity is characteristic for the Frank-van der Merwe (FM) growth mode (layer-by-layer growth) or the Stranski-Krastanov (SK) mode (monolayer growth followed by the three-dimensional cluster formation). Because of the lack of the plotted points at \(\geq 3\) min, we cannot determine whether the Na overlayer grows with the FM mode or the SK mode. However, it can be said that the two-dimensional Na overlayer with a monolayer thickness should be formed in the initial stages of adsorption (below 1.5 min). We define the kink point as \(\Theta_{Na} = 1\) monolayer (ML), and \(\Theta_{Na}\) is determined from the deposition time.

The atomic density of Na at 1 ML is roughly estimated to be \(2 \times 10^{15}\) atoms/cm\(^2\) by the following equation:

\[ N_{Na} = \frac{I_{Na1s} \sigma_{Zn1s}}{I_{Zn1s} \sigma_{Na1s}} 1 + \exp \left( -\frac{d_1}{\lambda \cos \theta_\lambda} \right) N_{Zn}, \]

This is derived from the model that the observed Zn 2p\(_{3/2}\) peak intensity of the clean surface \(I_{Zn1s}\) is given by the sum of the exponentially decaying intensities from each (10\(\bar{1}0\)) plane as a function of the distance from the surface. Here, \(N_{Na}\) and \(N_{Zn}\) are the densities of the Na adatoms and the Zn atoms in the (10\(\bar{1}0\)) plane \((N_{Zn} = 5.90 \times 10^{14}\) atoms/cm\(^2\)), respectively. \(\sigma\) is the photoionization cross section of the core level by Al K\(_\alpha\) radiation \((0.1165\) and 0.2605 Mb for Na 1s and Zn 2p\(_{3/2}\), respectively [14]). \(d_1\) and \(d_2\) are 0.0939 and 0.1878 nm, respectively, which correspond to the layer distances between the (10\(\bar{1}0\)) planes in the (10\(\bar{1}0\)) direction. \(\lambda\) is the inelastic mean free path of the Zn 2p\(_{3/2}\) electrons in ZnO and is 1.27 nm according to the TPP-2M equation [15]. \(\theta_\lambda\) is the detection angle of the photoelectrons \((0 \pm 10^\circ)\). The intensity of the Na 1s peak \(I_{Na1s}\) at the kink point is \(\sim 0.15\) with respect to \(I_{Zn1s}\) (Fig. 1c) so that we obtain \(N_{Na} = 2 \times 10^{15}\) atoms/cm\(^2\) at 1 ML.

In the submonolayer coverage region (\(\Theta_{Na} \leq 1\)), the line shape of the Na 1s peak is characterized by a Gaussian profile. However, the high-binding-energy tail is gradually developed at \(\Theta_{Na} > 1\) ML, and two peaks become observable at the higher binding-energy side of the main peak at \(\Theta_{Na} = 2.7\) and 6 ML. The tail structure, indicated by arrows in Fig. 1a, is due to development of the asymmetry profile of the Na 1s peak and is caused by the electron-hole pair excitation around the Fermi level in the
FIG. 1: (a) Na 1s and (b) Zn 2p$_{3/2}$ core-level spectra of the ZnO(10$ar{1}$0) surface covered with different amount of Na. In order to avoid contamination of the Na overlayer, freshly prepared Na deposited surfaces were subjected to the measurements for each Na coverage. The background-subtracted Na 1s peaks at $\leq$ 1 ML is fitted well by a single Gaussian (red lines) [The Shirley background is assumed (green lines)]. On the other hand, the Na 1s peaks cannot be reproduced by a single Gaussian at $> 1$ ML. Arrows in Fig. 5a indicate the high-binding-energy tail structure, and tick marks show the plasmon loss peaks. (c) Plot of the integrated intensities of the Na 1s and Zn 2p$_{3/2}$ peaks as a function of the deposition time. The peak intensity is normalized by the intensity of the Zn 2p$_{3/2}$ peak from the clean surface.

The Na-induced shift of the valence band should be due to downward bending of the ZnO band, because a similar shift to the higher binding-energy side upon Na adsorption is also observed in the Zn 2p$_{3/2}$ peak (Fig. 1b) and the O 1s peak (not shown). Adsorption of the electropositive species like AM’s on semiconductor surfaces induces downward bending of the substrate’s band [20–22], whereas the electronegative species such as oxygen and halogen lead to upward band bending [22–24]. Therefore, Na-induced downward bending of the ZnO band is an indication that the Na adatoms are positively charged on the surface in the initial stages of adsorption.

More direct evidence for ionization of Na is obtained from the measurement of the work function change ($\Delta \Phi$). The inset of Fig. 2 shows the deposition-time dependence of $\Delta \Phi$ (filled circles) and the band-bending corrected work

photoemission process [16]. On the other hand, the high-binding-energy peaks (the positions are marked by ticks) are separated by 5 and 10 eV from the main peak and are well ascribed to the single and double losses by the surface/bulk plasmon excitation within the metallic Na overlayers, because the surface and bulk plasmon loss energies of Na metal are 4.1 and 5.8 eV, respectively [16]. Thus, it is concluded that the Na overlayer gains a metallic nature at $\Theta_{\text{Na}} > 1$ ML. On the other hand, the Gaussian profile of the Na 1s peak in the submonolayer region suggests the nonmetallic nature of the Na adatoms. The change in the nature of the overlayer is also inferred from the shift of the Na 1s peak position. The Na 1s peak is observed at 1073.7 eV at 0.07 ML and shifts to 1073.0 eV at 6 ML. The peak shift should be caused by the change in the efficiency of the core-hole screening by valence charge of Na, \textit{i.e.}, the more sufficient screening is provided at high coverages because the itinerant electrons can participate to screen the core hole in the Na overlayer with the metallic property, whereas one electron at the most contributes to the screening in the nonmetallic phase.

In the nonmetallic phase at $\Theta_{\text{Na}} \leq 1$ ML, the Na adatoms is actually in a cationic state because Na adsorption induces (i) downward bending of the ZnO band and (ii) a sharp decrease in the work function of the ZnO(10$ar{1}$0) surface. Fig. 2 shows the change in the normal emission spectrum of the valence band of ZnO(10$ar{1}$0) as a function of the Na deposition time. The valence-band spectrum of the clean surface consists of the emissions from the O 2p–Zn 4sp hybrid bands at 3–8 eV and the Zn 3d bands at 10–11 eV [17, 18]. A peak at 3.8 eV is ascribed to the emission from the O 2p dangling bond state [19]. As the surface is being covered with Na, the dangling bond state is largely attenuated along with the overall shift of the valence band to the higher binding-energy side by 0.4–0.5 eV. The Na-induced shift of the valence band should be due to downward bending of the ZnO band, because a similar shift to the higher binding-energy side upon Na adsorption is also observed in the Zn 2p$_{3/2}$ peak (Fig. 1b) and the O 1s peak (not shown). Adsorption of the electropositive species like AM’s on semiconductor surfaces induces downward bending of the substrate’s band [20–22], whereas the electronegative species such as oxygen and halogen lead to upward band bending [22–24]. Therefore, Na-induced downward bending of the ZnO band is an indication that the Na adatoms are positively charged on the surface in the initial stages of adsorption.

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FIG. 2: The Na deposition-time dependence of the valence-band spectra of the ZnO(1010) surface. The photon energy used was 19.5 eV, and the photoelectrons emitted to the normal direction were corrected. The vertical bars indicate the position of the valence-band maximum. The shift of the valence-band maximum reflects downward bending of the ZnO band. The inset shows the work function change ($\Delta \Phi$) and the change in the ionization potential ($\Delta I$) as a function of the Na deposition time. The calibration of the deposition time has not been done so that the actual Na coverage is not known.

function change, i.e., the change in the ionization potential $\Delta I$ (filled squares). Unlike adsorption systems on metal surfaces, $\Delta I$ directly reflects the adsorption-induced dipole moment on semiconductor surfaces [25]. A sharp decrease in $\Delta I$ by $\sim 1$ eV up to 40 s means that a large dipole moment with the negative end being directed towards the bulk inside is formed. Thus, it is reasonable to conclude that the Na adatoms are ionized on the surface in the initial stages of adsorption.

From the above discussion, Na adsorption on ZnO(1010) is found to proceed via the ion-to-metal transition of the nature of the Na overlayer. The measurements of the Na KL$_{23}$L$_{23}$ Auger transition peak as a function of $\Theta_{Na}$ give more insight into the transition process of the overlayer’s property. Fig. 3a shows the Zn L$_{3}$M$_{45}$M$_{45}$ Auger spectra for (i) the clean, (ii) Na-covered ($\Theta_{Na} = 6$ ML) and (iii) 50-L O$_2$-exposed Na-covered ZnO(1010) surfaces (1 L = $1 \times 10^{-6}$ Torr-s). The Zn L$_{3}$M$_{45}$M$_{45}$ Auger peak is observed at 988.5 eV with a slight hump at 992 eV. Upon Na adsorption, the Na KL$_{23}$L$_{23}$ Auger peak appears at the higher kinetic-energy side of the Zn Auger peaks. From the difference spectrum [(iii) – (i)], the position of the Na KL$_{23}$L$_{23}$ Auger peak is determined at 994.8 eV, in good agreement with the corresponding peak of metallic Na (994.5 eV [26]). On the other hand, when the metallic Na overlayer is oxidized by dosing 50-L O$_2$, the Na KL$_{23}$L$_{23}$ peak shifts to 991.0 eV as shown in the difference spectrum [(iii) – (i)]. This value is close to the literature value for Na$_2$O, 990.0 eV [26], and thus the Na adatoms are oxidized by exposing to O$_2$.

With these kinetic energies of the Na KL$_{23}$L$_{23}$ peaks in mind, we will examine the $\Theta_{Na}$-dependent change of the Na KL$_{23}$L$_{23}$ spectrum from the submonolayer to multilayer region. Fig. 3b shows the differences between the spectra of the Na-covered surfaces and those of the clean surface. Dip structures at $\sim$ 988.5 and 992 eV are due to the attenuation of the Zn L$_{3}$M$_{45}$M$_{45}$ peaks as a result of scattering of the emitted Auger electrons by the Na overlayer. On the other hand, peaks at $> 990$ eV are attributed to the Na KL$_{23}$L$_{23}$ transition. In the submonolayer coverage region ($\Theta_{Na} < 1$ ML), the Na Auger peaks cannot be determined unambiguously because of the poor signal-to-noise ratio. However, two peaks, which are labeled A and A’, are observable at 991 and 993.7 eV at $\Theta_{Na} = 1$ ML. Increasing $\Theta_{Na}$ leads to a gradual development of peak A’ with respect to peak A. At high coverages ($\Theta_{Na} = 2.7$ and 6 ML), the Na KL$_{23}$L$_{23}$ emission is dominated by the peak at 995 eV, which is different from the position of peak A’. This peak is labeled B. Peak B should not be the shifted peak A’ but be formed by the newly developed emission, since a contribution of peak A’ is still seen as a shoulder of peak B at 1.7 and 2.7 ML. From the position of peak B (995 eV), it is related to the Na adatoms in a metallic phase. On the other hand,
FIG. 3: (a) Zn L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} and Na K\textsubscript{L23}L\textsubscript{23} Auger spectra of (i) the clean surface, (ii) the 6-ML Na-covered surface and (iii) the 50-L O\textsubscript{2}-exposed Na-covered surface. Upper two curves are difference spectra between the spectra (i) and (ii) and between (i) and (iii). (b) Na K\textsubscript{L23}L\textsubscript{23} Auger spectra of the Na-covered surfaces shown as difference spectra with respect to those of the clean surface.

The emission from the completely ionized Na species forms peak A. Peak A’ locates at slightly lower kinetic-energy side of peak B so that it should originate from the slightly ionized Na adatoms.

The Θ\textsubscript{Na}-dependent change of the difference spectrum implies that the Na adatoms in the metallic phase should be dominant at Θ\textsubscript{Na} ≥ 2.7 ML, whereas the Na cations are the main species at Θ\textsubscript{Na} ≤ 1.3 ML. This is a consistent result with that deduced from the Na 1s XPS measurements (Fig. 1a). However, an interesting finding in the AES measurements is that both ionic and metallic peaks are observed in the spectra at Θ\textsubscript{Na} = 1.7 and 2.7 ML. This means that the ionic and metallic Na phases coexist on the surface in this coverage region. From this observation, we propose that the Na adatoms in direct contact with the ZnO(10\textsubscript{1}0) surface are positively charged and the metallic phase is formed by the Na adatoms on top of the first Na layer, while the ionic state of the Na atoms in the first layer is intact. The origin of the differently charged Na cations is not clear at this moment, but it could reflect the different adsorption sites on the substrate surface, e.g., highly charged Na may result from the species directly bonded to the surface O atoms, while the Na adatoms in the vicinity of the surface Zn atoms should be slightly ionized.

The property of the Na overlayer on ZnO(10\textsubscript{1}0) is unique in that the ionic and metallic phases coexist on the surface. For many AM adsorption systems, the AM adsorption process is described as follows [27]: The deposited AM adatoms are ionized and form a dipole moment on the surface in the initial stages of adsorption. The increase in the AM coverage leads to a larger electrostatic repulsion between the adatoms because the AM–AM distance gradually decreases. In order to weaken the repulsive interaction, depolarization of the dipole moment proceeds by reducing ionic charge on each AM adatom. Finally, as the AM–AM distance becomes short enough to establish a direct valence-orbital interaction, the metallic band is emerged in the AM overlayer. Such an ion-to-metal transition is usually brought about before the completion of the first atomic layer so that the AM overlayer with coverages larger than a monolayer is metallic in nature. For the present Na/ZnO(10\textsubscript{1}0) system, on the other hand, the Na adatoms in the first layer are considered to remain ionic even though the metallic phase is formed on top of the first layer. Absence of the ion-to-metal transition in the submonolayer region has also been found for the K/ZnO(10\textsubscript{1}0) system [8]. Moreover, the Cs adatoms are proved to be in an ionic state at around the coverage of the completion of the first layer, as shown in the next section.

B. Cs adsorption state

Fig. 4 shows Cs 3d\textsubscript{3/2}, Zn 2p\textsubscript{3/2} and O 1s spectra of the clean ZnO(10\textsubscript{1}0) surface (bottom spectra) and the Cs-covered ZnO(10\textsubscript{1}0) surfaces before and after O\textsubscript{2} exposure (middle and upper spectra, respectively). The Cs coverage was estimated from the intensity of the Cs 3d\textsubscript{3/2} peak relative to that of the Zn 2p\textsubscript{3/2} peak of the clean surface using Eq. 1 with the corresponding parameters, i.e., the cross section of the Cs 3d\textsubscript{3/2} electron σ\textsubscript{Cs3d} = 0.22156 Mb [14] and the Cs 3d\textsubscript{3/2} peak intensity I\textsubscript{Cs3d} = 0.1. We obtain the density of the Cs adatoms to be (6–7) × 10\textsuperscript{14} atoms/cm\textsuperscript{2}, which is nearly equal to the density of
FIG. 4: The Cs 3d_{3/2}, Zn 2p_{3/2} and O 1s spectra of the clean ZnO(10\{0\}) surface and the Cs-covered surfaces before and after 10-L O\textsubscript{2} exposure. The Cs 3d_{3/2} peaks of two Cs-covered surfaces can be fitted by single Gaussian functions.

the surface Zn or O atoms on the ZnO(10\{0\}). Considering the atomic or ionic radius of Cs, this atomic density should correspond to the coverage which is close to the completion of the first atomic layer.

As shown in Fig. 4, the Cs 3d_{3/2} peak with a symmetric lineshape is observed at 740.9 eV. The background-subtracted peak can be reproduced by a single Gaussian function. The Gaussian profile of the Cs 3d_{3/2} peak is preserved when the Cs-covered surface is exposed to 10-L O\textsubscript{2}. This means that the adsorption state of the Cs adatoms is the same before and after the O\textsubscript{2} exposure. The lack of the plasmon loss feature and the metallic asymmetry profile in the Cs core-level peak is indicative of the non-metallic nature of the Cs overlayer at this coverage.

Cs adsorption induces the shift of both Zn 2p_{3/2} and O 1s peaks to the higher binding-energy side by 0.05–0.1 eV. The shift is attributed to Cs-induced downward band bending, although the magnitude of the shift is much smaller than that observed for the Na/ZnO(10\{0\}) system. Thus, it is assumed that the Cs adatoms are ionized on the surface.

Absence of the ion-to-metal transition of the AM overlayer before the completion of the monolayer on ZnO(10\{0\}) is common for the AM atoms investigated (Na, K and Cs). This is in marked contrast to the adsorption process of AM on many metal and semiconductor surfaces, on which the AM overlayer is transformed from the ionic state to the metallic state in the submonolayer coverage region. A driving force for the ion-to-metal transition is the increased dipole–dipole repulsion between the ionized adsorbates as the coverage increases [27]. Usually, the ion-to-metal transition of the AM overlayer is accompanied by weakening of the overlayer–substrate interaction, as evident from the thermal desorption experiments [28–30]. However, the AM adatoms are bound rather strongly to the ZnO(10\{0\}) surface because, as will be discussed in the next section, the temperature at which maximum desorption of Na and Cs at monolayer coverages takes place is 700–800 K, which is higher by 100–200 K than the desorption temperatures of Na and Cs on the metal surfaces [28–30]. Such a strong bonding may prevent the AM overlayer in direct contact with the ZnO(10\{0\}) surface from transforming from the ionic state to the metallic state.

It is important to mention that, although the decrease in the peak intensity and the shift of the peak position are brought about for the Zn 2p_{3/2} core level as the surface is covered with Na and Cs, the lineshape itself remains unchanged (Figs. 1b and 4). This suggests that the reduced...
Zn species are not formed on ZnO(10\(\overline{1}0\)) even though both Na and Cs are ionized and valence charge is transferred to the substrate. Such an observation is in sharp contrast to the results of the PES experiments for other AM/oxide systems such as K/TiO\(_2\)(110) [31], Na/TiO\(_2\)(110) [32] and Na/Fe\(_3\)O\(_4\)(111) [33], where the reduced metal species are observed as a shoulder structure at the lower binding-energy side of the main peak in the core-level spectra. For TiO\(_2\) and Fe\(_3\)O\(_4\), the metal d orbitals contribute to the lower part of the conduction bands, and thus transferred charge should occupy the metal d orbital. This means that transferred charge resides in the metal atoms on the substrate surface because of the localized character of the d orbitals. On the other hand, the bottom of the conduction band of ZnO is composed of the Zn 4s band [17] so that transferred charge occupies the Zn 4s orbitals. Because of the dispersing feature of the Zn 4s band, charge in the Zn 4s band can be delocalized over the surface region as well as in the subsurface region. Thus, the net gain of charge at each Zn ion becomes relatively small. Such a nonlocal charge transfer could be the reason why the reduced Zn species are not observed in the Zn 2p\(_{3/2}\) core-level spectra in the present AM/ZnO(10\(\overline{1}0\)) systems.

C. Effect of annealing

In this section, we show the effect of annealing on the Na and Cs atoms adsorbed on the ZnO(10\(\overline{1}0\)) surface. For some AM/oxide adsorption systems such as Na/Cr\(_2\)O\(_3\)(0001) [34] and K/Fe\(_2\)O\(_3\)(111) [35], diffusion of the AM atoms into the bulk upon annealing has been suggested. Thermally induced migration of adsorbed Na has also been proposed on the ZnO(000\(\overline{1}\)) surface [36]. However, we conclude that, by simply annealing the AM-covered surfaces as employed in the present work, diffusion of Na, K and Cs into the ZnO substrate does not take place on ZnO(10\(\overline{1}0\)). On the contrary, segregation of
The left and center panels of Fig. 5a show respectively the Cs 3d_{3/2} and Zn 2p_{3/2} core-level spectra taken at room temperature after annealing the Cs-covered ZnO(10\10) surface (6–7 \times 10^{14} \text{Cs/cm}^2) at various temperatures for 3 min. Both Cs 3d_{3/2} and Zn 2p_{3/2} peaks shift to the lower binding-energy side by 0.6–0.8 eV up to 600–700 K and to the higher binding-energy side at higher temperatures. Along with the peak shift, the intensities of these peaks vary with temperature as shown in the right panel of Fig. 5a; the Zn 2p_{3/2} peak intensity gradually increases and goes back to that of the clean surface by 1000–1100 K, whereas the Cs 3d_{3/2} peak diminishes to zero. Although the Cs 3d_{3/2} peak decreases from the low temperature region, the maximum decreasing rate is observed at 700–800 K. These observations mean that the desorption peak of Cs from ZnO(10\10) is 700–800 K and that desorption is completed by 1000–1100 K. Similar peak shift and intensity variation are also observed for the Na 1s and Zn 2p_{3/2} peaks for the Na/ZnO(10\10) system as shown in Fig. 5b. In the Na adsorption system, the Na 1s and Zn 2p_{3/2} peak intensities increase and decrease, respectively, with a significant change in the temperature region between 700 and 800 K, and the Na 1s peak is no more observable at 900–950 K.

The temperature-dependent change in the intensities of the Cs 3d_{3/2} and Zn 2p_{3/2} peaks and of the Na 1s and Zn 2p_{3/2} peaks seems to have a good correlation. They are indeed linearly correlated. As the Zn 2p_{3/2} peak intensity is plotted against the intensities of the Na 1s and Cs 3d_{3/2} peaks, as shown by filled triangles in Figs. 6a and 6b, respectively, it linearly increases with decreasing the AM core-level peak intensities. Furthermore, a linear correlation is emerged when Na and Cs are deposited on ZnO(10\10) at room temperature. The plot of the Zn 2p_{3/2} peak intensity obtained in the adsorption experiment is shown by filled circles. The same relation is also found for the K/ZnO(10\10) system. In Fig. 6c, the Zn 2p_{3/2} peak is plotted against the K coverage, which has been determined by the K 2p peak intensity [8], and thus against the K 2p peak intensity. All these results imply that thermally induced diffusion of the AM adatoms into the ZnO substrate is not operative, because the Zn 2p_{3/2} peak intensity should tend to be larger in the desorption process than in the adsorption process at a certain intensity of the AM core-level peak if bulk diffusion of AM occurs upon annealing.

As long as the change in the Zn 2p_{3/2} peak intensity is concerned, adsorption and desorption can be viewed as a reversible process. However, an irreversible process is apparent when we follow AM-induced band bending. As shown in Figs. 1b and 2, adsorption of Na on ZnO(10\10) leads to downward band bending so that the core-level and valence-band spectra shift to the higher binding-energy side. Cs adsorption also results in downward band bending (Fig. 4). On the other hand, the shift to the lower and then to the higher binding-energy side of the core levels is induced by annealing the Na- and Cs-covered ZnO(10\10) surfaces (Fig. 5). We consider the annealing-induced shift to be due to the change in bending of the substrate’s band. Namely, downward band bending on the AM-deposited surface at room temperature turns to upward bending as the surface is annealed.

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the AM adatoms simply desorb from the surface, such upward bending should not be observed.

In our previous study for K/ZnO(10\overline{1}0)\ [9], in which annealing-induced upward band bending has been observed, we propose, on the basis of the quantitative analysis of the O 1s core-level peaks, that upward bending results from accumulation of the O atoms which migrate from the bulk inside as the sample is heated to high temperatures. It is known that adsorption of the electronegative atoms such as oxygen and halogen on semiconductor surfaces induces upward bending of the substrate’s band [22–24]. This is the case for the O_2-exposed Cs/ZnO(10\overline{1}0) surface, where O adsorption induces the shift of all Cs 3d_{3/2}, Zn 2p_{3/2} and O 1s peaks (Fig. 4). Therefore, upward bending on the annealed AM/ZnO(10\overline{1}0) surface is due to the O adatoms, which diffuse from the bulk towards the substrate surface.

Annealing-induced accumulation of the bulk O atoms has been proposed to be operative even on the clean ZnO surfaces, because the bands bend upwards when the ZnO surface is measured at high temperatures [9, 11]. However, the accumulated O atoms should diffuse back to the substrate to recombine the O vacancies in the subsurface region as the surface is cooled, and upward bending is removed at room temperature [11]. On the AM-covered surface, on the other hand, a part of the accumulated O atoms cannot diffuse back to the substrate because they are bonded to the surface AM atoms. This is the reason why upward bending is observed even at room temperature for the AM-covered surfaces.

The annealing effect on the adsorbed AM atoms on ZnO(10\overline{1}0) is summarized as follows: The O atoms are accumulated on the surface from the relatively low annealing temperature and are bonded to the AM adatoms. This leads to upward bending of the ZnO band. The AM adatoms, which are oxidized by the accumulated O atoms, simply desorb from the surface. Diffusion of AM into the bulk is denied because the Zn 2p_{3/2} peak intensity depends only on the intensities of the AM core-level peaks regardless of the adsorption or desorption process. It is noted that the Zn 2p_{3/2} peak intensity seems not to be affected by the O atoms accumulated on the surface although they should contribute to suppress the Zn 2p_{3/2} peak intensity. We consider that such an effect should be smaller than that by the AM adatoms. Actually, the Zn 2p_{3/2} peak intensity decreases by less than 5 % when the Cs-covered surface is exposed by O_2 (Fig. 4), and this falls within the error of the peak intensity measurements. Thus, the Zn 2p_{3/2} peak intensity looks like to be only affected by the number of the AM adatoms in the present work.

D. LEED measurements

The LEED measurements show that, as Na and Cs are deposited on ZnO(10\overline{1}0) at room temperature, the (1\times1) spots from the substrate surface become blurred and the background intensity is increased. This indicates that Na and Cs adatoms do not form any long-range ordered superstructure. K adatoms deposited on ZnO(10\overline{1}0) at room temperature also do not form an ordered structure.

FIG. 7: LEED patterns of (a) the clean ZnO(10\overline{1}0) surface and the Na-covered surfaces annealed at (b) 780 K, (c) 825 K and (d) 860 K. The primary energies of the incidence electron beam are 70 and 40 eV for the clean and annealed surfaces, respectively.
FIG. 8: Schematic models of the c(2×2) and (1×3) structures by AM’s on ZnO(10\(\overline{1}0\)). The AM atoms are placed at the sites which the Zn atoms would occupy if the bulk structure repeats on top of the ZnO(10\(\overline{1}0\)) surface. The accumulated O adatoms, which diffuse from the bulk inside upon annealing, are not shown in these models.

[8]. In contrast, annealing the AM-covered surfaces results in some ordered structures. Fig. 7 shows the LEED patterns of (a) the clean ZnO(10\(\overline{1}0\)) surface and the Na-covered surfaces annealed at (b) 780 K, (c) 825 K and (d) 860 K. Up to 780 K, only a minor change in the LEED pattern is brought about as compared with the LEED pattern of the pre-annealed surface. As annealing temperature is increased to 825 K, the (1×3) pattern becomes observable (Fig. 7c). The fractional spots then turn to streak lines (Fig. 7d) before the (1×1) pattern is again obtained at 900–950 K, at which all Na adatoms are removed from the surface. Annealing-induced ordering of the adsorbates is also observed for the K/ZnO(10\(\overline{1}0\)) system [8], for which the c(2×2) LEED pattern is observed at the K coverage of a half monolayer (the atomic density of K is a half of the Zn or O density in the (10\(\overline{1}0\)) plane) and the (1×3) pattern at one-third of a monolayer. Contrary to these two systems, the Cs-covered ZnO(10\(\overline{1}0\)) surface do not give any LEED pattern even on the annealed surfaces at any temperature.

If the LEED patterns of the annealed Na- and K-covered ZnO(10\(\overline{1}0\)) surfaces originate from the ordered structures by adsorbed AM’s, and this hypothesis is plausible by the fact that the K coverages are 1/2 and 1/3 of the monolayer on the ZnO(10\(\overline{1}0\))-c(2×2) and -(1×3) surfaces, respectively [8], the models for the c(2×2) and (1×3) structures can be schematically drawn as indicated in Fig. 8. On the c(2×2) surface, which is formed only for the K adsorption system, the K adatoms are uniformly distributed over the surface with a quasi-hexagonal structure. On the other hand, the (1×3) structure should be composed of the K or Na adatoms, which form atomic chains with a 1× periodicity along the [1\(\overline{2}10\)] direction with an inter-chain distance of 1.56 nm. Formation of the highly anisotropic (1×3) structure by the Na and K adatoms must be largely owing to the unique structure of the ZnO(10\(\overline{1}0\)) surface, which is covered with the Zn–O dimer rows running parallel to the [1\(\overline{2}10\)] direction. Such an atomic structure may lead to thermal diffusion of the Na and K adatoms preferentially along the Zn–O dimer.
rows so that the atomic chain along the Zn–O dimer row is easily formed. The reason why a particular LEED pattern is not observed for the Cs adsorption system is not clear at this moment, but we speculate that the Cs–ZnO interaction is weaker than the Na–ZnO and K–ZnO interactions so that the Cs adatoms can diffuse more easily in the direction perpendicular to the Zn–O dimer rows. A weaker Cs–ZnO interaction relative to the Na–ZnO interaction is directly proved when we compare the temperature-dependent change in the intensities of the Cs 3d_{3/2} and Na 1s peaks (Fig. 5); although desorption of both Cs and Na is maximized at 700–800 K, Cs desorption starts from just above 300 K, whereas significant desorption of Na occurs at above ~600 K. Thus, thermal fluctuation should prevent the formation of the ordered Cs structures.

In the above discussion, the possible contribution of the thermally accumulated O adatoms to the observed LEED patterns is not referred. The K and Na adatoms in the c(2×2) and/or (1×3) phases are in a cationic state. Thus, coadsorption of cations with these cations should yield an electronically more stable surface than the surface without the anions. This is especially in the case of the (1×3) phase, because the K–K or Na–Na distance in the chain is only 0.325 nm so that the lateral dipole–dipole repulsion may be large enough to destabilize the chain structure. If the accumulated O adatoms adsorb on the AM chains, they should play a role to suppress the electrostatic repulsion to some extent, and the AM chain is consequently realized. It is for further study to determine the ordered structures including both AM and O atoms and to elucidate the role of the coadsorbed O atoms.

IV. CONCLUSION

PES and LEED are utilized to elucidate the electronic and atomic structures of the Na- and Cs-adsorbed ZnO(111) surfaces. Both Na and Cs atoms are in a cationic state when they interact directly with the ZnO surface. For the Na adsorption system, the metallic phase is developed on top of the first Na layer while the cationic state of Na in the first layer remains intact. Such an adsorption process is unique because, for many AM adsorption systems on metal and semiconductor surfaces, the ion-to-metal transition takes place in a submonolayer coverage region and the AM overlayer gains the metallic property at coverages larger than a monolayer. Persistence of the ionic nature of the AM adatoms in direct contact with the ZnO surface is also found for the Cs adsorption system.

On the Na- and Cs-covered surfaces, downward bending of the substrate’s band is induced, because valence charge is transferred from AM to ZnO and the adsorbed AM atoms are positively charged. On the other hand, strong upward band bending is observed on the annealed surface. Accumulation of the O atoms on the surface via segregation of the bulk O atoms should cause upward bending. Another effect of the heat treatment is the formation of an ordered overlayer. Although room-temperature desorption of Na results in the disordered overlayer at any coverages, the (1×3) overlayer is emerged on the annealed surface at 825 K. The ordered structure is considered to arise from the Na adatoms which form atomic chains along the Zn–O dimer rows. For the Cs adsorption systems, on the other hand, an ordered structure is not formed in both adsorption and desorption processes. The different behavior of Na and Cs may be due to the different strength between the Na–ZnO and Cs–ZnO interactions.

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