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Alkali-metal-induced satellite peaks associated with the K 3p and Al 2p core levels have been measured with photoemission for K/Al(111) and K/Al(100) under both low- and room-temperature preparation conditions. For low-temperature deposition we observed loss peaks in good agreement with electron-energy-loss spectroscopy studies of analogous systems which we assign to the excitation of collective plasmonlike modes in the alkali-metal overlayer. For room-temperature preparation conditions, we observed significant changes in the satellite loss structure which we attribute to a decrease or loss of metallic behavior in the alkali-metal layer. We account for some of our results as a change in bonding configuration of the K atoms from on-top-of surface to substitutional adsorption for low versus room-temperature preparations.

I. INTRODUCTION

In the past few years, quite a lot of interest has been generated in the properties of alkali-metal atoms adsorbed on aluminum single-crystal surfaces. Some of this renewal of interest stems from the determination for the Al(111) surface that many if not all of the alkali-metal atoms adsorb in either low-symmetry top sites (at low temperature) or in substitutional sites (at higher temperature) in neither case in the high-symmetry threelfold hollow sites which intuition had previously suggested. Substitutional adsorption has also more recently been reported for alkali metals/Al(100). In other words, alkali-metal adsorption on the aluminum surface is not the simple, classic free-electron-like system that had been assumed for decades.

Along with the significant interest in the geometric structure of these overlayers, a substantial number of both experimental and theoretical investigations of the electronic structure have also appeared over the past few years. Much of this work was carried out without knowledge of the unexpected geometry of these overlayers, particularly the transformation to substitutional sites at higher temperatures. As a result, the interpretations of some of these theoretical and experimental results may need to be reexamined. It is the purpose of the present study to investigate some aspects of the electronic properties of alkali metals/Aluminum, in particular, K/Al(100) and K/Al(111), with special attention to changes which occur upon transformation from supersurface (“normal” top or hollow sites) to substitutional bonding of the alkali-metal atoms. A further difference in alkali-metal adsorption between K/Al(100) and K/Al(111) which also may be reflected in our results is the fact that K forms islands on the Al(111) surface, vs uniform growth on Al(100).

One particular probe of the electronic structure of alkali-metal overlayers which has been applied to many systems over the years, including fairly recent studies of alkali metals/aluminum, is electron-energy-loss spectroscopy (EELS or ELS). Distinct loss peaks in the energy range of 1-6 eV have been observed for many different alkali-metal overlayer systems in both submonolayer and multilayer coverage ranges. For low coverages (below 1/3 of one alkali-metal layer) this peak in most cases is observed to decrease in loss energy as a function of increasing coverage. Over this coverage range it has generally been assigned as an alkali-metal interband transition or transition between alkali-metal atomic-like energy levels. For submonolayer coverages above approximately 1/3 layer, the loss peak in most cases stops decreasing in energy and then increases in energy as a function of increasing coverage up to the completion of the first layer. [EELS results of K/Al(111) (annealed) are actually an exception to this general behavior, as was discussed further below.] For one layer and above, the loss occurs at or very close to the plasmon energy of the alkali metal (at the surface and/or bulk plasmon energy depending on the film thickness). Partly for this reason the loss peak in the higher submonolayer coverage range is usually associated as a collective, plasmon or plasmonlike excitations in the alkali-metal layer.

In this investigation, we have investigated loss features analogous to those previously observed with EELS by studying satellite peaks associated with alkali-metal and Al core levels in photoemission spectra. Our results for low-temperature adsorption are in good agreement with the assignment of plasmon excitations based on EELS measurements of analogous systems for the higher submonolayer coverage range. For the alkali-metal layers either deposited at or annealed to room temperature (resulting in adsorption in substitutional sites) we observe significant differences vs low-temperature adsorption in the core-level satellite structure which we feel reflects the...
differences in the electronic structure of the alkali-metal overlayers in the different bonding configurations.

II. EXPERIMENT

The measurements reported here were carried out at the soft x-ray beamline 22 at the MAX-I storage ring in Lund, Sweden. This beam line is equipped with a modified SX-700 monochromator, a large hemispherical electron energy analyzer of Scienta design and featuring a multichannel detection system, and a multilevel UHV system equipped with a variety of surface science preparation and characterization instrumentation including a rear-viewing low-energy electron-diffraction (LEED) system whose images can be recorded by a video camera interfaced to a personal computer.

The Al(100) and Al(111) crystals were cleaned by Ar bombardment at a sample temperature of ~550 K, followed by annealing at ~700 K. The cleanliness was monitored by using photoemission to check the core levels of possible contaminants such as C and O. The base pressure in the measuring chamber was ~6×10^{-11} Torr. The samples were heated resistively by passing current through the two W wires which were used to support the crystals. These wires were attached to a Dewar which was filled with liquid N_{2} to cool the crystal (to ~90 K). The potassium dosing was performed by passing current through a SAES getter source, which had previously been thoroughly outgassed. Deposition rates were monitored and controlled by observing the alkali-metal signal in a mass spectrometer, and by recording LEED patterns and alkali-metal core-level photoemission spectra. The pressure rise during deposition was ~1×10^{-10} Torr. All measurements reported here were performed at liquid-nitrogen temperature.

III. RESULTS

A. K/Al(111)

In Fig. 1 is presented a series of photoemission spectra of K/Al(111) around the Al 2p core-level region (the peaks at ~73 eV binding energy) taken with an excitation energy of 110 eV. Changes in the Al 2p core levels as a function of alkali-metal coverage and annealing can be seen in Fig. 2, which is a full-scale presentation of the spectra from Fig. 1. These effects have already been well documented and will not be discussed further here.

The lower five spectra in Fig. 1 show a clearly defined satellite peak at ~2–2.5 eV below (at higher binding energy than) the Al 2p cores due to the adsorption of potassium at a sample temperature of 90 K. This peak grows in intensity with coverage, stays approximately fixed in energy for the lower three coverages, and then shifts to higher loss energy with increasing K coverage for the three higher-coverage spectra. We attribute the coverage independence of the loss energy for the lower coverages to the fact that K/Al(111) grows in islands at this temperature over this coverage range.

When the overlayer at a coverage of 0.33 ML is annealed to room temperature, the satellite peak shifts to lower loss energy (~1.5 eV), as shown by the topmost spectrum in Fig. 1. We have examined this annealing behavior in several sequences with similar results. It is difficult to ascertain if there are any changes in intensity or width of the loss peak upon annealing due to its position superimposed on the high-energy tails of the Al 2p core levels.

FIG. 1. Photoemission spectra of the Al 2p core-level region of Al(111) for a series of K depositions at 90 K as well as the results of an anneal of a 0.33 ML coverage to room temperature. The photon energy was 110 eV.

FIG. 2. The same photoemission spectra as displayed in Fig. 1 in a full-scale presentation.
B. K/Al(100)

In Fig. 3 is presented an adsorption sequence of K/Al(100) taken again around the Al 2p core-level region. A weak loss peak below the core (at ~74.5 eV binding energy) can be detected for a K coverage of 0.24 ML. This peak increases in intensity and binding energy (and therefore in loss energy) as the coverage is increased up to the approximate completion of the first alkali-metal layer. An analogous loss peak is also observed below the K 3p core levels and is presented in Fig. 4, which is from the same set of measurements as Fig. 3 for the Al 2p core region. (The K 3p core levels at 18–19 eV binding energy will be discussed in more detail in a future publication.)

A loss peak, which is not clearly distinguishable from the K 3p cores until a coverage of 0.36 ML, increases in intensity and binding energy as the K coverage increases. In Fig. 4 we also present the spectrum from a ~double layer of K/Al(100) (0.96 ML), where a strong loss peak near the surface plasmon energy of potassium (ωpK=2.7 eV) is observed. (This peak is quite broad and slightly asymmetric, probably due to contributions from surface, bulk, and interfacial plasmon excitations.)

In Fig. 5, we have plotted the loss peak positions obtained from several different K/Al(100) and K/Al(111) adsorption sequences, including those presented in Figs. 1, 3, and 4, as a function of K surface density. The peak positions plotted here have been estimated from the raw data without any background subtraction or line-shape analysis. This plot includes satellite peaks associated with the Al 2p core levels taken at a photon energy of 110 eV along with K 3p loss peaks taken with photon energies of 41, 43, 105, and 110 eV. The loss energy shifts more or less linearly vs coverage and is very similar to the results of most EELS studies of similar systems.

In Fig. 6 we present a series of photoemission spectra of K/Al(100) around the K 3p region as a function of K coverage for deposition at room temperature. Core-level measurements discussed elsewhere indicate a substitutional adsorption of the K on this surface under these conditions. As can be seen from this figure, even for coverages up to one monolayer of K, no new satellite peak is observed below the K 3p core levels. At best, there are rather subtle changes in the background shape and perhaps some filling in of the tail region.

FIG. 3. Photoemission spectra of the Al 2p core-level region of Al(100) for a series of K depositions at 90 K. The photon energy was 110 eV.

FIG. 4. Photoemission spectra of the K 3p core-level region of K/Al(100) for a series of K depositions at 100 K. The photon energy was 43 eV.

FIG. 5. The core-level satellite loss energy vs K surface density in units of $10^{15}$ atoms/cm$^2$ for K/Al(100) and K/Al(111). Data include losses off the Al 2p core levels taken with a photon energy of 110 eV, and losses off the K 3p core levels taken with photon energies of 41, 43, 105, and 110 eV. Also plotted are some of the results from an EELS investigation of K loss energy vs density for the system K/Ni(100) taken from Refs. 63–66. As a point of reference, the saturation coverages (densities in units of $10^{15}$ atoms/cm$^2$) for the three systems are as follows: K/Al(100), 0.5 ML (0.61); K/Al(111), 0.45 ML (0.846), and K/Ni(100), 0.38 ML (0.61).
FIG. 6. Photoemission spectra of the K 3p core-level region of K/Al(100) for a series of K depositions at room temperature. The photon energy was 90 eV.

**IV. DISCUSSION**

Our photoemission results clearly demonstrate the existence of satellite peaks below both the K 3p and Al 2p core levels for higher K coverages [above approximately \( \frac{1}{3} \) of a K layer (\( \theta > 0.25 \text{ ML} \)) for low-temperature deposition on the Al(111) and Al(100) surfaces. These peaks grow in intensity and shift to higher loss energy with increasing K coverage up to the completion of the first K layer, and are very similar in behavior to analogous EELS studies of alkali-metal overlayers. In Fig. 5 we have also plotted some of the results of loss energy vs density from an EELS study of K/Ni(100) by Andersson and Jostell.\(^6\) Our own results from core-level photoemission are in very good agreement with this study. This good agreement along with the similarities to other EELS studies lead us to make an assignment of the core-level satellite peaks in our own investigation as collective plasmon-like excitations in the K overlay. This is one of the first photoemission studies in which satellite peaks associated with core levels have been identified for submonolayer alkali-metal coverages.\(^7\) In several previous investigations, alkali-metal induced loss peaks below copper d bands, which may have a similar origin, have been reported.\(^8,9\)

The lowest potassium coverage for which we can clearly identify a satellite peak is \( \theta = 0.24 \text{ ML} \) (see Figs. 1 and 3). We do not observe a peak at half this coverage for K/Al(100) (\( \theta = 0.12 \text{ ML} \), bottommost curve in Fig. 3). Based on the weak intensity of the 0.24 ML peak for K/Al(100), we would not be sensitive to peaks at much lower coverages than this, particularly if the peak was to continue to shift to lower loss energy into the tail of the Al 2p core levels. It may be significant that we only observe this core-level satellite over the higher-coverage range in which the EELS loss peaks also increase in energy with coverage. For low coverages, for which a more atomic-like origin for these EELS losses is suggested, the probability of excitation by a core level may decrease, contributing to the lack of observation of core-level satellite peaks below \( \frac{1}{2} \) layer in our investigation. More careful studies at intermediate coverages are desirable in order to address this issue.

At this time we would like to emphasize the importance of the differences in growth between K/Al(100) vs K/Al(111). On K/Al(111), the K forms higher-density islands at relatively low coverage (~0.1 ML) at 100 K, which grow in size as the K coverage is increased.\(^6\) This growth reflects itself in our results in the more or less constant value of the loss energy observed at lower coverages (as seen in the lower spectra in Fig. 1). On the other hand, the K growth is more uniform on the Al(100) surface at 100 K, with a more or less constant increase in the average density of the K layer with coverage.\(^5\) This growth produces the monotonic increase in loss energy vs coverage or density which we have detected in this investigation.

Regarding the approximately linear dependence of the loss energy on coverage as displayed in Fig. 5, it is expected that the plasmon energy will increase with increasing electron density and therefore with alkali-metal coverage in the present cases under consideration. However, simple models predict square-root dependence on the electron density.\(^2\) The linear dependence on alkali-metal coverage observed here and elsewhere was discussed by Andersson and Jostell in their earlier work,\(^6\) but has still not been accounted for.

The results of a recent calculation by Ishida and Liebsch\(^4\) of electronic excitations in alkali-metal overlayers may also be relevant to a proper interpretation of our results. They find in the dynamic linear response of Na and K overlayers on a jellium substrate that collective excitations appear for higher submonolayer alkali-metal coverages approaching 1 ML. However, for low coverages below the work-function minimum, they only detect a broad loss peak in their calculations which is due to a combination of surface screening processes and matrix element effects. This seems to be consistent with our core-level photoemission results since we only detect a loss peak, which we interpret as some sort of collective excitation, for higher alkali-metal coverages approximately above the work-function minimum for cold K depositions on both Al(100) and Al(111).

Now we would like to turn in our discussion to the results from room-temperature deposition or annealing of potassium on the aluminum surfaces. In terms of the satellite structure associated with the core levels, our data reveal significant qualitative differences between the low- and room-temperature cases. When one layer of K is annealed to room temperature on Al(111) (see the topmost spectrum in Fig. 1), the satellite peak shifts to lower loss energy by ~1 eV (to a loss energy of ~1.5 eV). This loss energy is in good agreement with the results of an EELS investigation of K/Al(111) by Tsuei et al.\(^\text{23,67}\) In that study, the K was deposited at 100 K, then the sample was annealed to 240 K, which would induce a transformation
to a substitutional site,\textsuperscript{6,10,71} before the EELS spectra were recorded. A loss peak at \( \sim 1.5 \text{ eV} \) was observed over much of the submonolayer coverage range. Island formation can account for the coverage independence of the loss energy in both EELS and photoemission spectra. Continuing with our results, for room-temperature deposition of K/Al(100) (compare Fig. 3 to Fig. 6), the changes in the satellite structure were even more dramatic—no distinct satellite peak can be detected at any K coverage.

How do we explain the dramatic differences in the core-level satellite peaks for low- vs room-temperature preparations? Clearly, it is reasonable to associate these changes with the structural changes of surface vs substitutional adsorption. If we assume that the loss peaks in our investigation and in the EELS studies at higher coverages are due to collective excitations, then the increase in loss energy with increasing coverage can be attributed to an increase in electron density in the alkali-metal overlayer. If this is the case, the shift of the K/Al(111) loss to lower energy and the disappearance of the K/Al(100) loss for room-temperature preparations are consistent with our expectation that the alkali-metal atoms in the substitutional geometry are fairly well screened from each other, which would tend to diminish the metallic behavior associated with collective excitations of the alkali-metal layer. This more "atomiclike" behavior will be reinforced by the stronger bonding of the alkali-metal atoms to the Al substrate atoms as a result of the substitutional geometry.

Such changes in the electronic structure of the alkali-metal layers on aluminum at room temperature have been confirmed in a recent calculation of Na, K/Al(111) by Wenzien et al.\textsuperscript{32} They carried out a surface Green’s function calculation of these systems for on-top and substitutional adsorption to determine the surface band structure and surface charge density distribution. They found a significant difference in the charge density in the surface layers for on-top vs substitutional adsorption—an almost complete lack of occupied density of states for the alkali-metal layer in the substitutional case. This loss of the "metallicity" of the alkali-metal overlayer for substitutional bonding is confirmed by our photoemission measurements of the core-level satellite excitations as described in this paper.

We cannot at this time account for the differences between room-temperature measurements for K/Al(111) vs K/Al(100). All evidence points to a similar structural transformation in the K overlayers for both K/Al(111) and K/Al(100) from adsorption on top of the surface at low temperatures to substitutional adsorption at room temperature, either for adsorption at room temperature or postannealing the low-temperature overlay. We therefore expected more similar changes in the satellite structure.

\section*{V. CONCLUSIONS}

Alkali-metal-induced satellite peaks associated with the K \( 3p \) and Al \( 2p \) core levels have been measured with photoemission for K/Al(111) and K/Al(100) under both low- and room-temperature preparation conditions. For low-temperature deposition we observe loss peaks in good agreement with EELS studies of analogous systems which we assign to the excitation of collective plasmonlike modes in the alkali-metal overlayer. For room-temperature preparation conditions, we observe significant changes in the satellite loss structure which we attribute to a decrease or loss of metallic behavior in the alkali-metal layer in this bonding configuration. Many of our results can be explained by differences in adsorption site or growth mode for K on these surfaces under various conditions.

\textit{Note added in proof}. A recent EELS study of K,Cs/Al(111) by Kondoh and Nozoye [Surf. Sci. \textbf{329}, 32 (1995)] yields results which are consistent with those presented in this paper.

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