PHYSICAL REVIEW B VOLUME 52, NUMBER 3 15 JULY 1995-I

Evidence for an inhomogeneous–homogeneous transition in the surface local electrostatic potential of K-covered Al(100)

C. B. Weare, K. A. H. German,* and J. A. Yarmoff†
Department of Physics, University of California, Riverside, California 92521
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 31 March 1995)

Resonant neutralization probabilities for 2 keV ^{7}Li$^+$ singly scattered from Al and K surface atomic sites are measured from K-covered Al(100). At low K coverages (<0.03 ML), nearly all of the Li$^+$ ions scattered from K are neutralized, while neutral fractions ranging from 32 to 65 % are measured for scattering from Al. This indicates that the surface local electrostatic potential is laterally inhomogeneous. At higher K coverages, on the other hand, the neutral fractions for scattering from Al and K become nearly equal, showing that the inhomogeneities are greatly reduced. This represents direct experimental evidence of such a transition.

Alkali atoms interacting with metal substrates have long been considered to be model systems for studies of adsorption.[1] When alkali atoms are adsorbed onto a surface, a change in the surface local electrostatic potential (LEP) is induced as the charge is donated to the substrate. In the limit of low alkali coverages, the changes in the LEP can be thought of as arising from individual dipoles located at the adsorbate sites. Thus, the LEP for this surface is expected to be laterally inhomogeneous. As the coverage is increased, some charge is donated back to the adsorbates resulting in a reduction of the adsorbate dipole moments. This depolarization of the adlayer should result in a reduction in the inhomogeneities of the LEP with increasing alkali coverage. At the highest coverages, the LEP should be nearly homogeneous, ultimately approaching that of a uniform dipole sheet. This work presents an experimental study of such an inhomogeneous to homogeneous transition of the LEP.

Resonant neutralization (RN) of scattered 2.0-keV ^{7}Li$^+$ is employed as a site-specific probe of the LEP.[2,3] The RN of scattered Li projectiles is a function of the LEP above the scattering site. As the LEP is reduced, RN becomes more efficient. Since the LEP can vary at different scattering sites, the degree of RN can also depend on the trajectory. Thus, by measuring the fraction of Li particles neutralized for scattering from adsorbate and substrate sites independently, variations in the LEP associated with these sites are detected.

In the present study, the neutral fractions of Li$^+$ ions singly scattered from metal substrate and alkali adsorbate atomic sites are measured independently via the difference in the scattered energy. A large scattering angle, i.e., close to 180°, is used to facilitate the separation of the singly scattered ions from the multiple scattering background and to increase the relative separation between single scattering peaks so that scattering from the adsorbate and substrate can be more clearly distinguished.[4] Such an arrangement also allows for the detected particles to be collected in a direction close to the surface normal, which ensures that the potential probed by the RN process is that associated with a particular localized surface site.[5,6]

Spectra of scattered ions were collected in an ultrahigh vacuum chamber equipped with a ^{7}Li$^+$ source and both time-of-flight (TOF) and electrostatic energy analyzers. TOF spectra were collected with the incoming beam at normal incidence and the analyzer positioned 12° off normal in the direction of the [011] azimuth, giving a scattering angle of 168°. The incident-beam energy was fixed at 2.0 keV with an energy spread of $<0.2\%$. The incident beam was deflected across a 1.0 mm^2 aperture to produce 40-ns pulses of ^{7}Li$^+$ at a rate of 80 kHz. Scattered ions and neutrals were detected after traveling 1.3 m. The spectra of the total particle yield were collected with the entrance to the flight tube at ground, while the neutral particles were collected by placing a bias voltage on the flight tube entrance to deflect away ions. The front of the microchannelplate detector was held at ground to ensure that ions and neutrals were collected with equal efficiency. The spectra were converted from TOF to energy by calibrating the positions of the Al and K single-scattering peaks (SSP) to spectra obtained with the electrostatic analyzer.

The Al(100) surface was prepared by repeated cycles of 1-keV Ar$^+$ sputtering and annealing to 400 °C. Crystal alignment and overlayer symmetry were determined with low-energy electron diffraction (LEED). The K overlayer was prepared by exposing the clean surface at room temperature to a well-outgassed SAES getter. The purity of the surface, as well as the K coverages, were determined by Auger-electron spectroscopy (AES). The coverages were calibrated by depositing 0.4 ML of K on the Al(100) surface (where 1 ML is defined as the number of atoms on the bulk-terminated surface), which is characterized by a sharp, split $c(2\times2)$ LEED pattern,[7] and then measuring the K252/Al68 AES ratio. Changes in the work function with K deposition were measured by the energy shift in the secondary-electron cutoff generated by bombardment of the sample with a 200-eV electron beam. Further de-

0163-1829/95/52(3)/2066(4)/$06.00

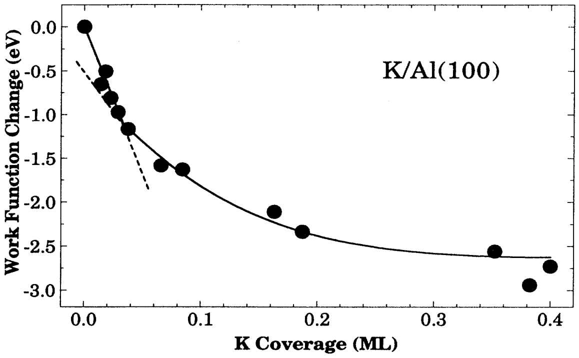

FIG. 1. Work-function change as a function of K coverage on Al(100). The dots are experimental data, while the solid lines show a fit to the data.

tails of the surface preparation are given in Ref. 8.

Figure 1 shows the relationship between the work function and K coverage. As K is first adsorbed, the work function is drastically reduced as a consequence of adsorbate-induced dipole formation. As the K coverage is increased beyond about 0.03 ML, the changes in work function with coverage are less extreme. Over the entire range, however, the relationship remains monotonic.

Representative energy spectra of $^7\mathrm{Li}^+$ scattered from Al(100) with a 0.4-ML K coverage are shown in Fig. 2 for the total yield and for scattered neutrals only. The Al SSP at ~670-eV results from elastic single scattering of ^{7}Li from isolated Al atoms. The K SSP, at ~940 eV, is due to single scattering from K. The background, which increases with decreasing scattered energy, arises from Li projectiles that have undergone multiple collisions.

The peaks labeled inelastic loss at ~640 eV in Fig. 2 result from particles, singly scattered from Al, that have lost energy via a charge promotion process from Li 1*s* to the Al Fermi level, which occurs during a fraction of the backscattering collisions, as explained in Refs. 8 and 9. This charge promotion forms an excited Li atom with a 1*s* hole that autoionizes away from the surface. Because the charge state of a projectile undergoing this process is not determined by RN alone, however, the neutral fractions associated with the inelastic loss feature should not be directly compared with the neutral fractions of the Al and K SSP's.

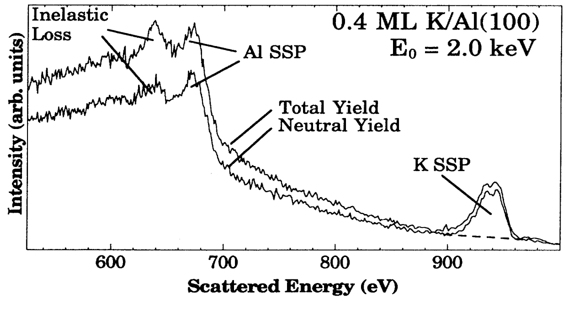

FIG. 2. TOF energy spectra collected at normal incidence for 2.0-keV $^7\mathrm{Li}^+$ scattered from 0.4 ML of K on Al(100).

Although the detailed shape of the background below the Al SSP is unknown, due to the complicating effects of the inelastic loss and to the complexity of the many possible multiple-scattering trajectories that can result in scattering at the SSP energy, it is still possible to determine a reasonable value for the neutral fraction of the singly scattered projectiles by assuming that the neutral fractions of the background and the Al SSP are equal. The neutral fractions of both the Al SSP and the multiple-scattering background represent averages over trajectories that sample the LEP at different points on the surface. Thus, in this method, it is assumed that the multiple-scattering trajectories sample regions of the surface with the same LEP as those sampled by the signal-scattering trajectories. This assumption is most accurate at both the lowest and the highest alkali coverages. At low coverages, most of the surface is bare Al, with only a few K sites. Therefore, the LEP is nearly uniform over most of the surface, so that most trajectories, with the exception of single scattering from K, probe the same LEP. At large K coverages, on the other hand, the inhomogeneity in the surface LEP has been greatly reduced (as discussed below). Thus, the neutral fraction is no longer dependent on the scattering site, and all trajectories probe approximately the same LEP.

To accurately calculate neutral fractions for the Al SSP, the average of the ratio of the neutral to total yields in a 30-eV window centered about the peak maximum was used. In this way, contributions to the Al SSP from trajectories that have undergone the charge promotion process are negligibly small. As is seen in Fig. 2, only a small fraction of the signal in this energy window comes from the inelastic loss feature. Furthermore, attempts to determine neutral fractions by first subtracting either linear- or spline-shaped backgrounds yielded values that were within 8% of that determined by the above method. Thus, the method is deemed adequate for the purposes of the present study.

The neutral fractions for single scattering from K sites were determined by simply dividing numerical integrals of the total and neutral yield K SSP's, following background subtraction. Background subtraction was straightforward for the K SSP because of the simple shape of the multiple scattering signal in this region, as seen in Fig. 2.

Figure 3 shows the neutral fractions of the Al and the K SSP's, determined as described above, as a function of the K-induced work-function change. The work-function change, rather than the K coverage, is used for the *x* axis since it provides a convenient way of comparing this data to models from the literature. Note that neutral fractions which exceed unity are simply a consequence of the scatter in the data, and the error bars do dip below 1.0. At coverages corresponding to work-function changes of less than 0.8 eV, Li projectiles that scatter from K are neutralized with near 100% efficiency, while the neutral fractions for scattering from Al sites are considerably less. As the coverage is increased, the K SSP neutral fraction drops by about 20%, while the Al SSP neutral fraction increases. At high coverages, the K and Al SSP neutral fractions are nearly equal.

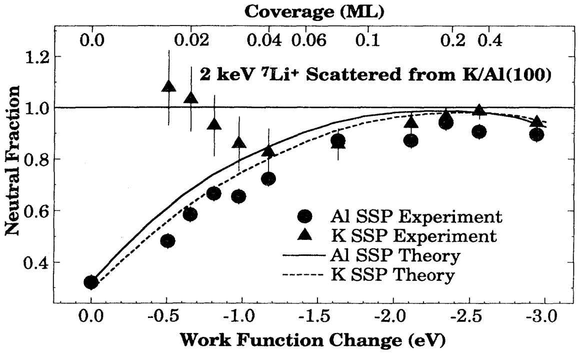

FIG. 3. Neutral fractions for 2.0-keV ^{7}Li$^+$ singly scattered from Al (●) and K (▲), shown as a function of K-induced work-function change. The corresponding K coverages are indicated at the top of the figure. The solid and dashed lines show the neutral fractions predicted by the model of Marston *et al.* (Ref. 10) for single scattering from Al and K.

For Li scattering from metallic surfaces, RN involves charge transfer primarily between the Li 2*s* level and the conduction band, and to a lesser extent, the 2*p* and affinity levels.[10] As the projectile approaches the surface, the projectile's electronic levels shift due to the image interaction and to any adsorbate-induced potential present. The levels also broaden as the projectile approaches the surface due to the coupling between the levels and the surface. Thus, the amount of overlap, and therefore the amount of charge transfer, between the levels and the conduction band depends on the distance above the surface, as well as on the LEP. The greater the overlap for a given distance from the surface, the greater the charge transfer.

As a scattered particle leaves the surface, the coupling between the projectile's electronic levels and the surface, and thus the probability for RN, falls off exponentially.[3] The charge state of a projectile is, therefore, determined at the distance from the surface at which the surface-atom coupling becomes negligible, which is referred to as the "freezing distance." In this way, only the exit trajectory is important in determining the final charge state of the projectile. For single scattering from Al, the freezing distance is calculated to be about 3.4 Å above the surface, using the method outlined in Ref. 3. While the freezing distance is, in principal, a function of the scattered velocity, the freezing distances for single scattering from Al and K are nearly equal because the difference in the final velocities for scattering from these sites is small. Note that in this simple interpretation of RN, charge exchange between the adsorbed and scattered alkali is not explicitly considered. Instead, the adsorbates are treated simply as perturbations to the LEP, i.e., any changes in the electronic structure caused by the alkali adsorbates are neglected.

For coverages corresponding to work-function changes of less than 0.8 eV (0.03 ML), K adsorption results in charge transfer from the adsorbate to the Al substrate. Thus, electric dipoles are formed at the K sites and the work function is reduced. Since the average separation between K adsorbates is large at these coverages, the LEP is highly corrugated, with the lowest potential located at the K sites. This low potential at the adsorbate sites results in a large overlap between the 2*s* level of the exiting Li and the occupied levels of the conduction band. As a consequence, RN is highly efficient for trajectories which scatter from K, resulting in almost total neutralization. At the Al sites, on the other hand, the LEP is higher, so that RN is less efficient, resulting in much lower neutral fractions.

As the alkali coverage is increased to coverages corresponding to work-function changes greater than 0.8 eV, the potential due to the surrounding dipoles acts to reduce the potential at an individual adsorbate site.[11] This reduction causes the valence level of the adsorbate to drop in energy relative to the Fermi level, thereby increasing the overlap between the valence level and the occupied portion of the conduction band. This, in turn, causes a donation of charge back to the adsorbate and a subsequent depolarization of the adsorbate layer. In Fig. 1, this is observed as a reduction in the magnitude of the slope of the work-function change vs coverage. The effect on the RN process is observed as the neutral fraction of the K SSP decreases from near unity to ~80% for work function changes between −0.8 and −1.2 eV, which shows that the LEP above K sites has indeed increased, i.e., the dipole moment of the adsorbates has decreased.

This sudden reduction in the dipole moment of the adsorbates may be the result of changes in the adlayer geometry. Core-level photoelectron spectroscopy studies of Na and K on Al(111) (Ref. 12) concluded that condensation of the adlayer occurs at ~0.1 ML. LEED studies of Li on Be(0001) (Ref. 13) and Na on Cu(111) (Ref. 14) revealed a transition from a disordered to a condensed phase on these surfaces, as well. In addition to the LEED observations in Ref. 13, occupied and unoccupied states were studied with photoelectron and inverse photoelectron spectroscopies, respectively. From these studies, it was concluded that the Li 2*s* level underwent a discontinuous transition from unoccupied to metallic at a coverage corresponding to the condensation transition observed with LEED. Similar results were reported in Ref. 14 for Na on Cu(111). This sudden change in the occupation level is attributed to the sudden increase of the depolarization field that results from the decrease in K-K separation.

An increase in the occupation of the alkali valence level will decrease the dipole moment of the adsorbates, resulting in an increase of the LEP near the adsorbate sites. As a consequence, resonant charge transfer will become less efficient, thereby reducing the neutral fraction for single scattering from an adsorbate. In this manner, condensation of the adlayer would result in a reduction of the neutral fraction of the K SSP, as is seen in Fig. 3.

For K-induced work-function changes of more than −1.2 eV (0.05 ML), the neutral fractions of the Al and K SSP's become nearly equal, which suggests that the inhomogeneities in the LEP have been greatly reduced. This is not meant to assert that the LEP is uniform at the adsorbate sites, but rather that the LEP at the freezing distance above the surface, i.e., on a scale of the order of ~3 Å, has become nearly homogeneous. To first order, this distance can be compared to the K-K nearest-neighbor distance at the transition coverage. If a uniformly distributed 0.05-ML adlayer is assumed, this distance is ~13 Å. However, this does not take into account islanding, which acts to reduce the effective K-K nearest-neighbor distances. Thus, the K-K nearest-neighbor and freezing distances become comparable to each other after a condensation of the adlayer.

To compare the data of the present study to a detailed theory of resonant charge transfer, the calculations shown in Fig. 3 were performed using the program developed by Marston *et al.*[10] These calculations include charge transfer to the 2*s*, 2*p*, and affinity levels of the Li ion. Note that a homogeneous LEP is assumed in these calculations, so that the only difference between scattering from Al and K sites is in the final velocities of the projectiles.

The calculations show qualitative agreement with the Al SSP data at all coverages and with the K SSP at high coverages. For the K SSP at low coverages, however, the agreement is very poor. Over the entire range, the theory predicts nearly equal neutral fractions for scattering from K and Al sites. However, for work function changes of less than 1.2 eV, the measured neutral fractions for scattering from K sites are significantly higher than for Al. This discrepancy arises because the calculations do not account for lateral variations in the LEP. At the higher coverages, however, the data and calculations do show good agreement. This agreement is expected as the LEP has become nearly homogeneous.

In summary, the work presented here is a measurement of the evolution from an inhomogeneous to a nearly homogeneous LEP as a function of alkali coverage. TOF spectroscopy allows for the direct measurement of the neutral fractions of the scattered Li projectiles. By measuring the scattered energy and charge state of projectiles that exit near the surface normal after undergoing large-angle single collisions, separate neutral fractions for scattering from substrate and adsorbate sites are obtained. The results presented here clearly show that the neutralization behavior of Li^+ scattered from Al and K sites differ as a function of K coverage. At low coverages, the LEP is laterally inhomogeneous, yielding different neutral fractions for scattering from Al and K. As the K coverage increases, however, a reduction in the neutral fraction for scattering from K sites is observed. This reduction may result from a condensation of the adsorbate layer. At the highest K coverages, the inhomogeneities in the neutral fractions, and therefore in the surface LEP, are greatly reduced as the K adsorbates form a nearly uniform dipole layer.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

[*] Present address: Battelle Pacific Northwest Laboratories, P.O. Box 999, Richland, WA 99352.

[†] Author to whom correspondence should be addressed.

[1] *Physics and Chemistry of Alkali Metal Adsorption,* edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[2] J. Los and J. J. C. Geerlings, Phys. Rep. **190**, 133 (1990).

[3] G. A. Kimmel and B. H. Cooper, Phys. Rev. B **48**, 12 164 (1993).

[4] Th. Fauster, Vacuum **38**, 129 (1988).

[5] K. A. H. German, C. B. Weare, P. R. Varekamp, J. N. Andersen, and J. A. Yarmoff, Phys. Rev. Lett. **70**, 3510 (1993).

[6] L. Jiang, Y. D. Li, and B. E. Koel, Phys. Rev. Lett. **70**, 2649 (1993).

[7] J. Paul, J. Vac. Sci. Technol. A **5**, 664 (1987).

[8] K. A. H. German, C. B. Weare, and J. A. Yarmoff, Phys. Rev. B **50**, 14 452 (1994).

[9] K. A. H. German, C. B. Weare, and J. A. Yarmoff, Phys. Rev. Lett. **72**, 3899 (1994).

[10] J. B. Marston, D. R. Andersson, E. R. Behringer, and B. H. Cooper, Phys. Rev. B **48**, 7809 (1993).

[11] T. Aruga and Y. Murata, Prog. Surf. Sci. **31**, 61 (1989).

[13] J. N. Andersen, E. Lundgren, R. Nyholm, and M. Qvarford, Surf. Sci. **289**, 307 (1993).

[13] G. M. Watson, P. A. Brühwiler, H. J. Sagner, and K. H. Frank, Phys. Rev. B **50**, 17 678 (1994).

[14] N. Fisher, S. Schuppler, Th. Fauster, and W. Steinman, Surf. Sci. **314**, 89 (1994).