Electronic-Structure Modification and the Adsorption Site of Oxygen on Alkali (Cs) Covered Surfaces Studied by Normal Exit Li^- Ion Spectroscopy

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(Received 18 June 1996)

Electronic-structure change of Ni(111) surfaces with low and high Cs precoverages upon exposure to oxygen has been studied by normal exit Li^- ion spectroscopy. It is shown that for low Cs coverages the Li^- yield from Ni sites decreases more rapidly than from Cs; while for Cs coverages near 1 monolayer (ML), both the yields show a maximum at low O exposures, which is explained as the extension of alkali valence-electron wave functions further towards the vacuum. The results also provide the first direct evidence that oxygen atoms lie above the Cs sites for Cs coverages near 1 ML and low O exposures. [S0031-9007(96)01313-0]

PACS numbers: 79.20.Rf, 34.70.+e, 73.20.At, 82.65.Pa

Coadsorption of alkali metal and oxygen on metal and semiconductor surfaces has attracted great interest as a prototype in investigating the promotion of catalytic reactions, the formation of negative-electron-affinity (NEA) surfaces, etc. [1]. One of the most interesting aspects is that the electronic structure modification by oxygen coadsorption shows a switch in behavior from low to high alkali precoverages [2–6]. Although it has been agreed that the alkali valence states play a key role in these physical processes, there is still a lack of understanding of the microscopic electronic structure and the adsorption site of oxygen [2].

In the literature, various spectroscopies, such as UPS and metastable deexcitation spectroscopy (MDS) [7–11], have been employed to probe the occupied local density of the valence-electron states (LDOS) of alkali and oxygen coadsorbed surfaces. UPS is less effective as the photoexcitation cross section is very low for the alkali valence s level. Moreover, UPS has a finite information depth and usually exhibits pronounced contributions from bulk states. In contrast, MDS is a technique of much higher surface sensitivity. However, Woratschek *et al.* concluded that MDS does not directly reflect the local density of states at a specific atom site, but rather the valence-electron states "seen" by an approaching atom at a distance of 3–5 Å from the surface where the deexcitation of incident He* 1s holes by the surface valence electrons occurs [11].

As a surface analytical technique, low energy ion scattering (LEIS) has an overriding advantage of extreme surface specificity. LEIS can not only directly provide the information on the position of surface atomic cores in real space, but it can also probe the local charge states of adsorbed surfaces. The neutralization of scattered D^+ or Li^+ ions with an exit path near the surface normal has been used to probe the local charge states of alkali covered surfaces at very low coverages [≤ 0.25 monolayer (ML)] [12,13], but no positive signals could be detected at higher alkali coverages due to the complete neutralization of the ions (throughout this paper 1 ML is defined as one close-packed alkali overlayer, the saturation coverage at room temperature). Although a time of flight (TOF) detector can be used to measure the neutral fraction, the neutralization occurs usually at a distance of 2–5 Å from the surface at high coverages, as the ionic (2s) level is well below the Fermi level of the alkali covered surface. In contrast, the formation of a Li^- ion in the outgoing trajectory is limited within a very small distance from the surface image plane due to the smallness of the affinity energy (0.62 eV) of a Li atom [14]. Thus atomic-site-specific Li^- ion spectra produced by low energy Li^+ ion scattering can be employed to probe the local density of valence-electron states by selecting an exit path (nearly) normal to the surface, provided that the delocalization of valence states, i.e., the metallization of the alkali overlayer, has not occurred on the surface [14], which occurs normally at alkali coverages ≥ 0.6 ML [15].

In this Letter, we report the first negative ion spectroscopy study of the electronic structure of alkali and oxygen coadsorbed surfaces. The results to be presented are for the oxidation of Cs covered Ni(111) surfaces. It is shown that at the initial oxygen adsorption, the Li^- yields from Ni and Cs sites are decreased for a low Cs precoverage of about 0.4 ML, but the yield from Ni is decreased more rapidly than from Cs; while both the yields from Ni and Cs are increased for a high Cs precoverage of nearly 1 ML. The former indicates that the impinging oxygen reacts predominately with Ni sites, while the latter is attributed to the wave functions of the alkali valence electrons extending further towards the vacuum caused by oxygen adsorption. Most strikingly, the present results provide the first direct evidence for the atop site of oxygen adsorption on alkali covered surfaces at low oxygen exposures, disproving the previously assumed subsurface site [2–4].

Detailed descriptions of the apparatus used have been published previously [10]. The base pressure of the ultrahigh vacuum (UHV) chamber was 7×10^{-11} Torr, and while the ion beam was on the pressure was kept below 1.5×10^{-10} Torr. The UHV chamber was equipped with a thermally activated Li^+ ion source, which produces a very stable Li^+ beam. The Ni(111) sample was cleaned by repeated cycles of 1 keV Ne^+ sputtering at 1 μA followed by annealing to about 900 °C. The surface cleanliness was checked by work function (WF) and 1 keV He^+ ISS measurements. Cs was evaporated from a thoroughly outgassed SAES getter source, and during evaporation the chamber pressure was kept below 4×10^{-10} Torr. Alkali coverages were determined by WF measurements. The WF change $\Delta\phi$ was measured by monitoring the shift in the low-energy threshold of the secondary-electron emission normal to the surface [14]. The energy spectra of electrons and Li^- ions were detected with a hemispherical electrostatic energy analyzer. The incident angle of Li^+ ions was 70° relative to the surface, and Li^- spectra were recorded at a fixed scattering angle of 160° (the surface normal). All the experiments were performed at 300 K.

Li^- energy spectra from Cs covered Ni(111) surfaces with various Cs precoverages were measured after exposure to increasing amounts of oxygen. The Li^- spectra for two different Cs precoverages ($\theta_{\mathrm{Cs}} = 0.4$ and 1 ML) are shown in Fig. 1. It is shown that the single scattering peak from Ni atoms is on top of a large background due to multiple scattering, similar to Li^+ spectra observed at low alkali coverages [16]. The integrated peak areas were obtained by subtracting a linear background under each peak [16]. In Fig. 2, the Ni and Cs peak areas versus oxygen exposure were normalized to their respective peak areas at zero oxygen exposure. The uncertainty in peak areas was within 5%. The results in Figs. 1 and 2 clearly exhibit the following features: For $\theta_{\mathrm{Cs}} = 0.4$ ML, the Li^- yield from Ni sites decreases sharply as the oxygen exposure is increased, whereas the yield from Cs sites decreases less rapidly; for higher θ_{Cs} near 1 ML, both the Li^- yields from Ni and Cs initially increase, pass through maxima, and then decrease to nearly zero with increasing oxygen exposure. It is interesting to note that for $\theta_{\mathrm{Cs}} = 1$ ML all data points of the normalized peak areas from Cs are below those from Ni, contrary to the case for $\theta_{\mathrm{Cs}} = 0.4$ ML. The WF changes as a function of oxygen exposure are shown in Fig. 2, in agreement with the switch behavior from low to high Cs precoverages reported by others [2–6].

For $\theta_{\mathrm{Cs}} = 0.4$ ML, the rapid reduction of the Li^- yield from Ni sites indicates that the impinging oxygen reacts drastically with the Ni substrate, capturing the valence charge from Ni sites. The charge transfer from Cs sites to oxygen is less efficient because most of the Cs valence electrons at low coverages are transferred to the substrate [14]. This result is consistent with those obtained by UPS and MDS, which show that for $\theta_{\mathrm{Cs}} \leq 0.5$ ML most of the oxygen atoms interact with the substrate, and some bind also to alkali adsorbates [9,10]. Apart from the drastic reaction of oxygen with Ni atoms, the shadowing of Ni sites by oxygen is another factor resulting in the more rapid decrease of the Li^- yield from Ni.

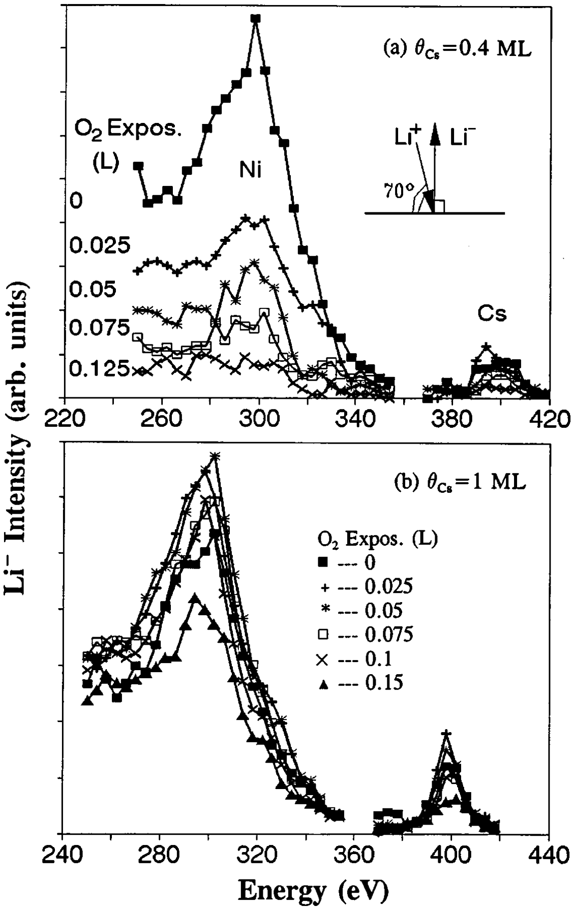

FIG. 1. Normal exit Li^- energy spectra from Ni(111) with (a) 0.4 ML and (b) 1 ML Cs precoverage after increasing exposure to O_2, obtained with 0.5 keV Li^+ incidence. The detection geometry is shown in (a).

For θ_{Cs} near the saturation coverages (1 ML), the present results are very interesting. In particular, both the Li^- yields from Ni and Cs show a maximum as a function of oxygen exposure. The similarity in the change of the two Li^- peaks is not unexpected, as for Cs coverages above 0.5 ML the wave function overlap between neighboring Cs atoms delocalizes the surface electronic states in the direction parallel to the surface [13–15]. In the literature, Woratschek *et al.* [7] first observed an initial increase of MDS intensity in exposing a thick Cs film of at least ten layers to oxygen, and explained it as being due to a quantum size effect of the conduction electrons as proposed by Burt and Heine [17]. Woratschek *et al.* [7] reported no such effect for oxygen exposure on a thin Cs layer ($\theta_{\mathrm{Cs}} = 1$ ML). The quantum-size-effect model assumed that the clusters of $\mathrm{Cs}_{11}\mathrm{O}_3$ are formed upon admission of O_2 onto the thick Cs film, and that the O^{2-} ions are buried in the interior of each cluster. In this structure, the wave functions of conduction electrons leak further into the vacuum due to the repulsion of the O^{2-} ions. The absence of such

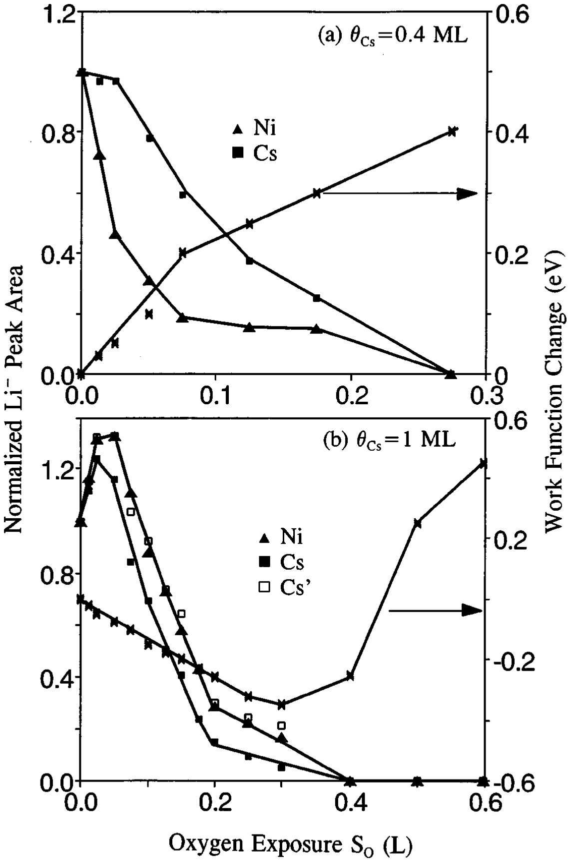

FIG. 2. Ni and Cs integrated peak areas normalized by their respective values at 0 L and the WF change versus O_2 exposure S_O. The data points ☐ in (b) are the normalized Cs peak areas ■ after correction by the screening factor $(1 - kS_O)$ with $k = 2.5\ L^{-1}$.

an effect in oxidizing a Cs monolayer was attributed to the absence of $Cs_{11}O_3$ clusters, which require at least three Cs atomic layers [7]. Subsequently, however, Nishigaki *et al.* [8] found such an effect on K covered Si(100) at $\theta_K = 1$ ML and explained it by the valence-electron redistribution at the vacuum side of K atoms induced by the initial oxygen adsorption. So far, we have observed this effect for admission of O_2 onto Cs covered Pt(111) [18], Cs-Si(100) [19], and the present Cs-Ni(111) surface with a Cs precoverage near 1 ML using Li^- ion spectroscopy. This effect is found to be a rather universal behavior. We find that the maximum of the Li^- yield appears at a very small oxygen exposure (<0.1 L) for $\theta_{Cs} = 1$ ML, compared with that for the thick Cs film (~0.3 L) [7]. This can be attributed to the lower valence-electron density of the thin layer than that of the thick film. The "absence" of the initial increase in MDS intensity for a Cs monolayer on a Cu(110) surface is likely due to the large oxygen dose increment (0.2 L) used (see Fig. 4 in [7]).

The change of the Li^- yield cannot be simply related to the WF change induced by oxygen. First, the Li^- yield maximum does not correspond to the WF minimum, as shown in Fig. 2(b). Second, the formation of Li^- ions on the outgoing trajectory along the surface normal depends essentially on the local valence-electron distribution and its density. Here we ascribe the initial increase of the Li^- yield to the wave functions of the valence electrons in the oxidized monolayer extending further towards the vacuum than in the pure Cs layer, as revealed in the MDS studies [7,8]. The extension of the wave functions increases the distance over which the electron capture to the Li atoms may occur, which thus enhances the Li^- yield. The wave function extension towards the vacuum caused by oxygen adsorption is, however, a puzzling phenomenon on account of the fact that $Cs_{11}O_3$ clusters are very unlikely to form on these monolayer covered surfaces. Thus there may exist an unknown underlying mechanism responsible for this striking electronic-structure modification.

The initial WF reduction of an alkali covered surface by oxygen adsorption is traditionally explained in terms of the formation of alkali-oxygen dipoles [2,4–6,8]. In order to produce the required dipole, it must be assumed that the oxygen atoms penetrate into the Cs layer with their sites below those of Cs, i.e., on sublayer sites. This assumption, however, was not based on the direct spectroscopic evidence, but from indirect results of AES, UPS, LEED, MDS, and other techniques [2–8]. As noted by Rhead [2], there is little information on the precise site of oxygen atoms on alkali covered surfaces, although the terms "sublayer" and "underneath" adsorption have been used. Thus the examination of the oxygen site becomes critically important.

Since experiments have shown that for alkali precoverages above 0.5 ML, ions scattering from substrate sites feel the same potential as those from Cs sites [11,12], the peak intensity change should be identical for both Li^- peaks from Ni and Cs. On the other hand, the shadowing of the surface atoms by oxygen atoms will modify the peak intensity variation, leading to a difference between the two peak variations. If one assumes that the oxygen atoms penetrate under the Cs layer, sitting at sublayer sites, they would shadow the substrate Ni atoms seen by the incident Li ions, but not the topmost Cs atoms. This assumption is in conflict with the results shown in Figs. 1(b) and 2(b). The results indicate that the Cs atoms are shadowed by the oxygen atoms seen by the Li^+ ions at the near normal incidence. After correction by the shadowing factor $1 - kS_O$, where k is a constant and S_O is the oxygen exposure, the data points for Cs fit those for Ni very well with $k = 2.5\ L^{-1}$. There is no quantitative AES analysis of the oxidation of a Cs monolayer, but such an analysis of the oxidation of a Ba monolayer covered surface indicates that the work function reaches its minimum when the stoichiometric Ba-to-O atom ratio is approximately 1-to-1 [at ~0.5 L of O_2 for Ba monolayer on W(100) surface] [20]. If this is also true for the oxidation of a Cs monolayer surface, the constant $k = 2.5\ L^{-1}$ (i.e., the Cs to O ratio is 1-to-1 at the exposure of 0.4 L) seems very reasonable, in view of the fact that the WF minimum occurs at the exposure of 0.3–0.4 L here. Strikingly, this result shows that the oxygen atoms are adsorbed above the Cs atoms, contrary to the previously assumed subsurface sites [2–4]. Moreover, if the oxygen were below the Cs sites and the Cs $6s$ valence electrons were transferred to the O $2p$ level as assumed in the dipole model, the wave functions of the Cs valence electrons would accumulate toward the substrate. This is in conflict with the observations by MDS [8] and the present Li$^-$ ion spectroscopy. Woratschek *et al.* [7] reported that no emission from the O $2p$ level was detected on the MDS spectra for the thick Cs film at low O exposures, which was used to indicate the incorporation of oxygen atoms below the Cs layer. However, the MDS O $2p$ peak appears appreciably for the surface covered with 1 ML of Cs even with low O exposures [7–10]. Thus we think that the MDS results [7–10] are not in conflict with the main conclusion drawn from the present Li$^-$ spectra, i.e., oxygen atoms occupy the atop sites of the Cs monolayer at low O exposures.

The above results lead to an unexpected conclusion that oxygen atoms on the alkali saturated Ni(111) surface are adsorbed on atop sites. This is similar to the case for oxygen adsorption on Al and Mg surfaces. The WF reductions observed on these surfaces were initially interpreted as being due to the penetration of oxygen atoms to the subsurface sites [21]. Recently, however, the actual adsorption site of oxygen on the Al(111) surface has been determined by various techniques and has been unanimously identified as the atop site, excluding the assumed subsurface site [22,23]. A similar conclusion has also been reached by Esaulov *et al.* for oxygen on Mg surfaces [24]. These results are surprising to those who believe in technique mechanism of the dipole model for the WF lowering. However, Zhang [25] has severely criticized the dipole theory for the WF change.

The present results imply that there are some exciting features associated with the drastic electronic-structure modification of the alkali precovered surface by oxygen. We would like to note the fact that oxygen or halogen adsorption on simple-metal surfaces, including alkali metals, alkaline-earth metals, and Al, is strongly nonadiabatic, leading to the adsorbate-surface system ending up with an excited state rather than the ground state [10,26–28]. These nonadiabatic processes manifest themselves by emission of exoelectrons and exophotons from the surface during adsorption [10,26–28]. Moreover, theoretical calculations [29] predicted and experiments [30,31] have confirmed that there are occupied and unoccupied discrete valence-electron states (the "quantum-well" states), respectively, lying in energies below and above the Fermi level for monolayer or multilayer of alkali metals on metal substrates due to the confinement of alkali conduction electrons within a thin layer. Thus it is probable that the nonadiabatic adsorption of oxygen on an alkali-monolayer covered surface leads to an excitation of electrons from occupied states to unoccupied states above the Fermi level, forming localized excited surface states, which can be stable because of the existence of the energy gap and the large lattice relaxation induced by the oxygen adsorption [32,33]. This conjecture is supported by our experimental results about low-energy secondary electron spectra from the alkali overlayer, which show that the subsequent oxygen adsorption creates a new peak below the low-energy edge (the vacuum edge), i.e., produces an occupied state between the Fermi level and the vacuum level. The results will be presented and discussed in a forthcoming paper [19].

One of the authors (Q. B. L.) acknowledges the financial support from the Department of Industry, Science and Trade (DIST) of Australia and the hospitality of NIRIM (Tsukuba, Japan) during his visit. The authors thank Dr. Y. Hwang for his help in processing the data.

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