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Interaction of oxygen with a Cs-monolayer-covered Si(100) surface

Q. B. Lu
Department of Physics, The University of Newcastle, Callaghan, New South Wales 2308, Australia

R. Souda
National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

D. J. O'Connor and B. V. King
Department of Physics, The University of Newcastle, Callaghan, New South Wales 2308, Australia

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Oxygen adsorption on a Cs-monolayer-covered Si(100) surface has been studied by Li^- ion spectroscopy and normally emitted secondary electron emission (SEE) spectroscopy. It is clearly shown that the oxygen lies above and below the Cs atoms, respectively, at low and high O exposures, disproving the dipole model for the work function change. The initial O adsorption induces a shoulder at the low-energy edge of the SEE spectra, indicating the existence of patches of a lower work function on the surface. The patches are explained as due to the CsO^* complexes formed by nonadiabatic chemisorption. [S0163-1829(96)51048-9]

It is well documented that the adsorption of oxygen on an alkali-metal-covered metal or semiconductor drastically modifies the electronic structure of the surface. One of the striking features is that the work-function (WF) change as a function of oxygen exposure shows an initial drop to a minimum followed by an increase to a nearly constant value, quite different from the WF behavior for oxygen adsorption on most of the bare substrates. The low WF surface plays a key role in many technological applications such as negative-electron-affinity (NEA) electron emitters and catalytic reactions.[1] The traditional explanation for this effect is the dipole theory, which assumes that at low exposures the oxygen atom, after capturing one electron, is incorporated into the alkali overlayer, sitting below the alkali ion and thus forming a positive-outward dipole field, while at high exposures the oxygen lies about the alkali, forming a negative-outward dipole. This assumption, however, was not based on the direct spectroscopic evidence, but from indirect results of low-energy electron diffraction (LEED), Auger electron spectroscopy, and ultraviolet photoemission spectroscopy (UPS)/x-ray photoemission spectroscopy.[2,3] It is worth noting that a recent study of the adsorption of oxygen on the Na-Al(111) surface using normal incidence standing x-ray wave-field absorption leads to an ''unusual'' behavior, i.e., the oxygen occupys the atop site of the surface Na atom.[4] Indeed, there is little information on the precise adsorption site of oxygen on alkali-covered surfaces.[2,3] It is well known that the structural information derived by LEED intensity analysis involves complicated model calculations, and therefore is rather indirect. In contrast, low-energy ion scattering (LEIS) is a technique of extreme surface sensitivity, and provides direct information on the positions of surface atomic cores in real space only using a simple concept of shadowing.[5] In our recent experiments using Li^- ion spectroscopy, we have demonstrated that at low exposures the oxygen lies at the top site, rather than the sublayer site, on the Cs-monolayer-covered Ni(111) surface.[6] This result strongly disproves the dipole theory. Zhang[7] has previously questioned the validity of the dipole model for the WF reduction.

Since alkali-metal valence states are considered to play a key role in varying the WF and in promoting catalytic reactions, various spectroscopies, mainly UPS and metastable deexcitation spectroscopy (MDS), have been employed to probe the occupied valence-electron states of alkali and oxygen coadsorbed surfaces.[8–10] UPS is less effective as the photoexcitation cross sections are very low for alkali valence levels. MDS has a much higher sensitivity than UPS, but the electron emission near the Fermi level E_F may result from the deexcitations of $He^*(2\,^1S)$, $He^*(2\,^3S)$, and $He^{*-}(2\,^2S)$, whose excitation energies in free atoms are rather close to each other (20.6, 19.8, and 19.4 eV, respectively).[11] At low O exposures, the initial intensity increase of a broad electron peak near E_F was interpreted as the wave functions of the conduction electrons extending further into the vacuum or the redistribution of the valence electrons at the vacuum side of the alkali atoms.[8,9]

The investigation of the energy distribution of low-energy secondary electrons might be of importance to understanding the local electronic structure of a surface, in particular, by applying the angle-resolved technique. The pronounced fine structure imposed on the low-energy cascade maximum is determined by the local density of surface electronic states, from which electrons are emitted. It is well known that for the surface with a homogeneous electrostatic potential, the minimum kinetic energy measured by an analyzer, i.e., for those electrons which have an energy just surmounting the vacuum barrier on the surface, equals Φ_S-Φ_A+eV_b, where Φ_S and Φ_A are, respectively, the WF's of the surface and the analyzer, and V_b is the bias voltage applied between the surface and the analyzer. Thus, the low-energy edge of the secondary electron emission (SEE) spectrum will shift downwards in energy with the decrease of the surface vacuum barrier (the surface WF). On the other hand, if there are some patches of different WF values on the surfaces, additional fine structure will appear in the low-energy edge of the SEE spectrum.

In this study, we present Li$^-$ spectra and normally emitted SEE spectra from 500-eV Li$^+$ ion scattering off the Cs-monolayer-covered Si(100) subjected to various O exposures. The purpose of this study is to examine the adsorption site of oxygen and to investigate the local electronic structure of the surface. The present Li$^-$ spectra demonstrate again that the oxygen lies above the Cs sites at low exposures, leading to a significant shadowing of Cs by O, while the reverse is the case at high oxygen exposures. Most strikingly, the SEE spectra clearly show a shoulder at about 0.4 eV below the main low-energy edge for low O exposures, which is attributed to the formation of excited CsO* complexes induced by nonadiabatic chemisorption.

Experimental details have been described previously.[6] The ultrahigh vacuum chamber had a base pressure of 7×10^{-11} Torr, and was equipped with a very stable Li$^+$ ion source. The Si(100) (p-type, 6–8 Ω cm) sample was carefully cleaned by flashing to about 1200 °C. The surface cleanliness was checked by WF and 1-keV He$^+$ ISS measurements. Cesium was evaporated from a thoroughly outgassed SAES getter source, and the saturated coverage at room temperature, i.e., one complete monolayer (ML), was determined by WF measurements. The energy spectra of Li$^-$ ions and emitted electrons were detected with a hemispherical electrostatic energy analyzer operating at energy resolutions of 4.0 and 0.2 eV, respectively. The Li$^+$ incident angle was 30° relative to the surface, and Li$^-$ spectra were recorded at a scattering angle of 60°.

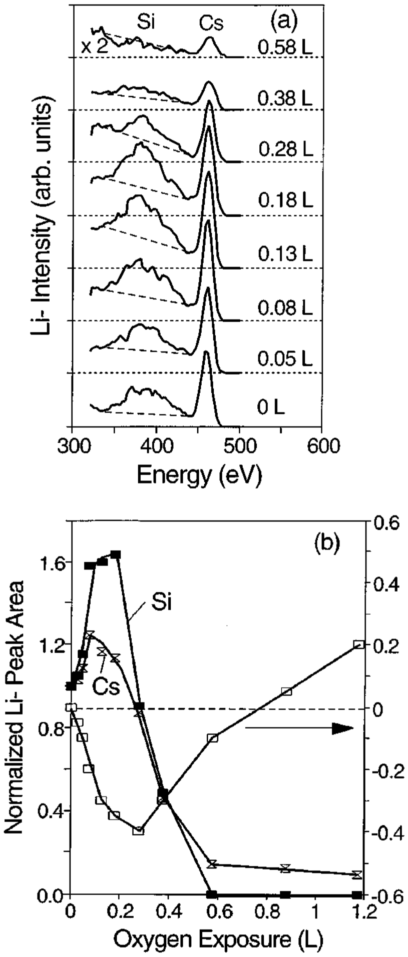

FIG. 1. (a) Li$^-$ energy spectra from the 1-ML Cs-covered Si(100) with increasing oxygen exposure, obtained with 0.5-keV Li$^+$ ion beam at the incident angle of 30° and the scattering angle of 60°; (b) Si and Cs integrated peak areas normalized by their respective values at 0 L and the WF change $\Delta\Phi$ versus oxygen exposure.

Li$^-$ energy spectra from the Cs-monolayer-covered Si(100) surface after exposure to increasing amounts of oxygen are shown in Fig. 1(a). Similar to the Li$^+$ spectra observed at low alkali coverages,[12,13] the single scattering (SS) peak from the substrate (Si) atoms is on top of a large background due to multiple scattering and is much wider than the SS peak from the Cs atoms. It is well known that the energy width of a scattering peak in a LEIS spectrum is determined by several factors, including the energy spread ΔE_1 of the primary ion beam, the energy resolution ΔE_A of the analyzer, the acceptance angle (i.e., angular resolution ΔE_N) of the analyzer, and the thermal vibration (ΔE_Γ) of surface atoms. For most LEIS apparatuses, the energy spread of a scattering peak results mainly from the latter two factors, which depend on the mass of the surface atom for an incident ion beam and a certain scattering angle and can be calculated on the basis of the binary collision model.[5] It is calculated that for Li$^+$ ion scattering at the scattering angle of 60°, $\Delta E_N(\mathrm{Si}):\Delta E_N(\mathrm{Cs})\approx 4:1$ and $\Delta E_T(\mathrm{Si}):\Delta E_T(\mathrm{Cs})\approx 1.2:1$, due to the much smaller mass of Si than that of Cs. Thus, the overall energy spread ΔE of the SS peak from Si being much larger than that of the SS peak from Cs can be expected, in good agreement with the spectra observed. The integrated peak areas of Si and Cs were obtained by subtracting a linear background under each peak. In Fig. 1(b), the Si and Cs peak areas versus oxygen exposure were normalized to their respective peak areas at zero oxygen exposure. The uncertainty in peak area was within 5%. Here, the pronounced feature is that the Li$^-$-yield maximum from Cs only increases by 25% compared with the yield for the fresh Cs monolayer and appears at an oxygen exposure of about 0.08 L ($1\ \mathrm{L}=1.0\times10^{-6}$ Torr s), while the Li$^-$ yield maximum from Si increases by 60% and corresponds to a larger exposure of 0.18 L. Moreover, the Li$^-$ yield from Si decreases sharply near the WF minimum at about 0.28 L and disappears at oxygen exposure $\geqslant 0.6$ L; whereas the Li$^-$ yield from Cs decreases slowly after the WF passes through its minimum and remains visible even up to the exposure of 1.2 L. Ignoring the origin of the WF lowering for the time being, the Li$^-$ intensity variation with oxygen exposure can then be simply assigned to the two counteracting effects: the great reduction in the surface valence-electron density and the appreciable decrease in the WF. Since for a high alkali coverage near 1 ML ions scattering from substrate sites feel the same potential as those from alkali sites especially with a near-glancing outgoing trajectory,[12–14] the different behavior between the changes of the Li$^-$ yields from Si and Cs must be attributed to the physical effect of shadowing by oxygen. The increase in the Li$^-$ yield from Si at the maximum is very close to the increase (65%) of the electron emission maximum near E_F in MDS spectra for K-monolayer-covered Si(100) surface adsorbed by oxygen,[9] while the Li$^-$ yield

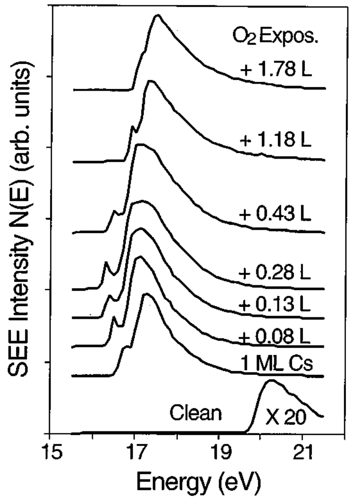

FIG. 2. Secondary electron spectra $N(E)$ emitted normal to oxidized Cs-covered surfaces for a 0.5-keV Li^+ ion beam incidence, with -19 eV applied to the sample.

maximum from Cs is significantly lower than this value. The results described above indicate that at low oxygen exposures $\leqslant 0.3$ L, i.e., before the WF passes through its minimum, the oxygen atoms lie above the Cs atoms and thus shadow mainly the Cs sites ''seen'' by the incident Li^+ ions; whereas at higher oxygen exposures >0.3 L, the additional oxygen atoms may position at the interstices between Cs atoms, shadowing the substrate Si sites severely. These results are clearly in conflict with the oxygen adsorption sites assumed in the dipole model,[15] which would result in no shadowing of the Cs sites but only the Si sites at low oxygen exposures.

Normally emitted low-energy SEE spectra $N(E)$ produced by 500-eV Li^+ incidence, under the fixed bias voltage of about -19 eV applied to the sample, are shown in Fig. 2. There is clearly only one sharp threshold edge on the spectrum for the clean Si(100) substrate. The whole spectrum for the Cs-monolayer-covered surface shifts left by about 2.9 eV, because the WF decreases from about 4.8 eV for the clean Si substrate to about 1.9 eV for the 1 ML Cs-covered surface. A small shoulder appears in the spectrum for the Cs-covered surface, which is due to the small oxygen contamination during evaporation of Cs, as the peak is negligible for the clean Cs-monolayer-covered surface observed in our other experiments performed in another chamber with a better vacuum ($\leqslant 2\times 10^{-11}$ Torr).[14] It is difficult to determine the intensity of the shoulder as a function of oxygen exposure as it strongly overlaps with the major edge, but it can be clearly seen that the shoulder grows with the increase of oxygen exposure, having a maximum in peak area at about 0.28 L where the WF reaches its minimum. With higher O exposures, the component of the shoulder decreases, corresponding to an increase in the WF. Finally, the shoulder disappears at O exposures $\geqslant 2.0$ L, and the WF increases to a saturation value near that of Cs oxide. These results clearly show that the WF change is closely related to the shoulder induced by oxygen. Similar results have been reported by Surnev, Rangelov, and Kiskinova in retarding potential I-V curves (the diode method).[16] The two thresholds in the SEE spectra for the oxidized surfaces demonstrate that there exist two vacuum barriers for emitted electrons over the surfaces. Both edges shift with the change of the average WF of the surface. The shoulder may be taken as evidence for the formation of patches on the surface, which have a lower WF than the other areas.

Then, a question arises immediately concerning the origin of the lower WF of the patches. The results on the adsorption sites of oxygen on the Cs-covered surface strongly indicate that the low WF patches cannot be assigned to the local Cs-O dipoles assumed previously. In addition, the oxidation of thick (i.e., bulk) Cs films has been intensively studied by Ertl and co-workers.[8,17,18] They proposed that the oxidation proceeds via the formation of suboxides with the $Cs_{11}O_3$ cluster to peroxide Cs_2O_2 and finally to the superoxide CsO_2.[17] The initial work-function reduction was attributed to the formation of $Cs_{11}O_3$ clusters,[8] in which the three O^{2-} ions formed by capturing six Cs valence electrons are buried in the interior of each cluster and are highly repulsive to the conduction electrons composed of the remaining five Cs valence electrons. The confinement of the conduction electrons to the outer region of the cluster raises their momentum and hence the Fermi energy (equivalently lowers the work function), as first proposed by Burt and Heine.[19] The formation of $Cs_{11}O_3$ clusters, however, is very unlikely for the present case, i.e., for the oxidation of the Cs-monolayer-covered surface.[8] One might propose other clusters such as Cs_2O to be formed during oxidation, but there is no physical basis for such a cluster to have a work function lower than that of pure cesium. In fact, the structure of the oxidized Cs-monolayer-covered Si(100) NEA surface is well ordered with a sharp (2×1) LEED pattern observed, indicating that clusters are not formed on this surface.[15] These facts compel us to look for a new possible mechanism.

It is interesting to note that the adsorption of highly electronegative adsorbates (halogen of oxygen) on alkali overlayers is strongly nonadiabatic, i.e., part of the reaction exothermicity is transferred into electronic excitation of the system.[17,18,20,21] As proposed by Nørskov, Newns, and Lundquist the reaction between a highly electronegative gas and an alkali surface may end up in an excited intermediate state, namely, a homopolar excited AX state (A is alkali and X highly electronegative atom).[20] The deexcitation of some AX complexes leads to the emission of electrons and photons from the surface. The emission probability has been observed to lie in the order of 10^{-5}–10^{-9} per oxygen-surface collision, which is much lower than that in gas phase reactions (10^{-2}–10^{-5}).[21] This, on the other hand, may imply that there exists a certain probability of the excited AX complexes being long lived on the surface. It is worth noting that excited impurity (defect) centers like O^* in a semiconductor bulk have an unusually long lifetime (persisting for hours, or even days), which was attributed to a large lattice-relaxation mechanism.[22,23] In the present case, a large lattice relaxation induced by oxygen adsorption is very likely to occur on the alkali-covered surface because of the strong attractive interaction between oxygen and alkali and the associated weakening of the lateral interaction between alkali atoms. Thus, a long lifetime of the excited CsO^* state on the surface might be expected as well. The valence electrons in the CsO^* complexes lie at an energy above the Fermi level, and thus feel a smaller vacuum barrier, which is responsible for the lower

WF. Thus, the proposed mechanism can explain the patches of a lower WF observed. Moreover, the formation of the excited CsO^* state can also account for the valence-electron wave functions extending further toward the vacuum caused by the initial oxygen adsorption, as shown in MDS spectra[8,9] and Li^- ion spectra.[6] This mechanism is further supported by the fact that for the adsorption of oxygen on alkali, alkaline-earth, and Al metal surfaces, where highly nonadiabatic reactions have been observed,[17,18,20,21] an initial WF reduction was generally found, while for the oxygen adsorption on the other metals, only a monotonic WF increase was observed. The adsorption site of oxygen on Al and Mg surfaces has been identified to be the atop site at low oxygen exposures,[24–26] which is also in conflict with the expectation from the dipole model and in agreement with the present observations. The feasibility of a long-lived excited state existing on an alkali and oxygen coadsorbed surface is based on the two facts: (i) the reaction is highly exothermic; (ii) an extremely large lattice relaxation at the surface is expected, creating a high enough barrier to deexcitation of the state.

In summary, we have clearly demonstrated that the oxygen adsorbate lies above the Cs at low O exposures, while the oxygen situates below the Cs at high O exposures for Cs and O coadsorbed Si(100) surface. These results are clearly contrary to the assumption in the dipole model. It has also been shown that a shoulder appears in the low-energy edge of the secondary-electron spectrum from the surface, which indicates that there are some patches having a lower work function than the other areas on the surface. The low WF patches have been interpreted as the formation of excited CsO^* complexes due to the nonadiabatic adsorption of oxygen on alkali-metal-covered surfaces. Although we have proposed a possible mechanism for the existence of the shoulder peak, we would like to note that the explanation of the origin is far from conclusive. We hope that this study will stimulate more detailed experimental studies by other techniques, e.g., photoelectron spectroscopy using synchrotron radiation with low-incident photon energies.

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