

ALKALI-METAL-AFFECTED ADSORPTION OF OXYGEN ON W(110)

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The oxygen attack of a W(110) surface partially covered by sodium or cesium was followed by Auger spectroscopy (AES), work function measurements, and LEED studies.

The work function exhibits remarkable changes as a function of the oxygen exposure. For small amounts of oxygen offered a work function decrease proportional to the alkali precoverage is observed. The results obtained in this range of oxygen exposures are explained by the formation of an oxygen sublayer underneath the prior adsorbed alkali atoms.

A rapid work function increase occurs for longer oxygen exposure. The magnitude of this increase is also correlated with the degree of the alkali precoverage.

1. Introduction

Alkali metals are widely employed in modifying surface properties [1,2]:

(1) Catalysts for surface reactions are often “promoted” by alkali metals in order to obtain a superior reactivity or selectivity of the catalyst. One example related to this work is the oxidation of ethylene on silver.

(2) Electron emission of metals and semiconductors can be strongly influenced by changes in the surface electronic structure and by the lowering of the surface potential barrier.

(3) Coadsorption of an alkali and oxygen on tungsten leads to a dramatic increase of the rate of production of excited Li-atoms in collisions of Li^+ -ions with such surfaces [3].

The coadsorption of Li-atoms and oxygen is by no means a new subject (see refs. [1,2,4–6]). Systematic studies of the oxygen adsorption on partially alkali (Li, K, Cs) covered Ag(111) as a function of the alkali coverage in the submonolayer range are available [7,8]. Our investigations are concerned with the oxidation of alkali (Na, Cs) covered W(110).

2. Experimental

The characterization of the prepared surfaces by AES, LEED, and work function measurements was performed in an ion-pumped standard apparatus

for surface diagnosis (model TNB-X of Perkin Elmer) bakable at 250 °C. The base pressure obtained using an ion pump supported by a LN₂ cooled sublimation pump is lower than 2×10^{-11} Torr.

The system consists of a cylindrical mirror analyzer (model 10–155 of Perkin Elmer), a four-grid LEED optics (model 15–120 of Perkin Elmer), and a quadrupole mass spectrometer (Extranuclear model 270–9) used here for residual gas analysis. Work function measurements were carried out with the electron gun of the LEED system using the diode method (reproducibility: ± 0.05 eV, typically).

Alkali atoms are deposited onto the cleaned W(110) crystal from a SAES Getters source. The procedure of cleaning the crystal is described in ref. [13]. Measurements as well as alkali deposition were conducted with the W(110) crystal maintained at room temperature. At this temperature only one layer of Cs can be deposited onto the substrate corresponding to a particle density of $(5.2 \pm 0.3) \times 10^{14} \text{ cm}^{-2}$ [9]. In conformity with most authors we use the term “monolayer” and the unit “ML” for the first complete adlayer. The degree of coverage in terms of 1 ML is estimated by following the ratio of the Cs auger signal to the W auger signal which shows a sharp kink when the monolayer is completed. For Na adsorption, the procedure is the same using the fact that the build up of the second layer does not start before the first monolayer (denoted by 1 ML) is completed. The completion of the first monolayer and the beginning of the second layer produces a kink in the ratio of the Na auger signal to the W Auger signal. We used this kink to estimate the degree of coverage for the Na adsorption. The particle density of one monolayer of Na on W(110) is $8.5 \times 10^{14} \text{ cm}^{-2}$ [10]. The calibration of the alkali coverage in terms of alkali monolayers is estimated to be accurate within ± 0.05 ML.

Oxygen admission is made from a bakable stainless steel gas inlet system through a precisely controlled leak valve. The gas admission system was baked out in regular time intervals. The purity of the admitted gas was monitored by means of the quadrupole mass spectrometer.

3. Results

Fig. 1 shows the variation of the work function ϕ due to the oxygen adsorption on partially cesiated W(110) at different Cs precoverages (θ_{Cs}). Curve a is the variation of the work function for the adsorption of Cs on W(110) alone. The abscissa given is in units of the Cs saturation coverage (1 ML). The other curves show the work function change upon oxygen exposure to the partially cesiated surface for different values of θ_{Cs} . The initial Cs coverage is given with the respective curve. The scale for the oxygen exposure is shown in langmuirs (L). The origin of the oxygen exposure scales are displaced according to the respective Cs precoverage. For all values of θ_{Cs}

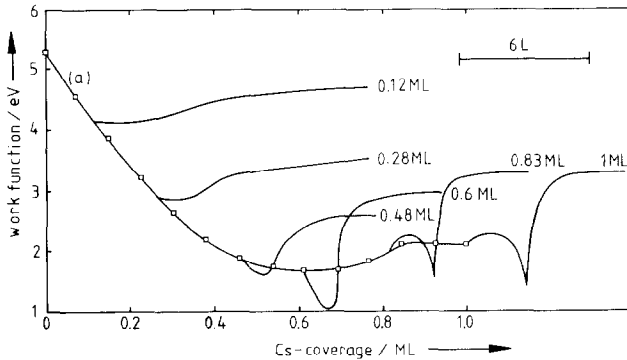


Fig. 1. Variation of the work function of a partially cesiated W(110) surface as a function of the oxygen exposure. See explanations given in the text.

there is an initial decrease of the work function towards a minimum during oxygen exposure. This minimum becomes more pronounced with increasing θ_{Cs} . Beyond the minimum a rise of ϕ is found which becomes rather pronounced for $\theta_{Cs} > 0.3$ ML. For larger Cs coverages the minimum is essentially confined to oxygen exposures < 6 L. The slow rise of the work function at oxygen exposures > 6 L which is especially seen for $\theta_{Cs} < 0.3$ ML is attributed to oxygen adsorption at alkali-free sites.

The magnitude of the work function decreases with respect to the initial, un-oxidized value obtained for the partially cesiated surface, $\delta\phi_m$, is plotted in fig. 2a as a function of the initial Cs-coverage. For $\theta_{Cs} > 0.2$ ML the variation is of the form

$$\delta\phi_m = c(\theta_{Cs} - \theta_0)^n, \quad (1)$$

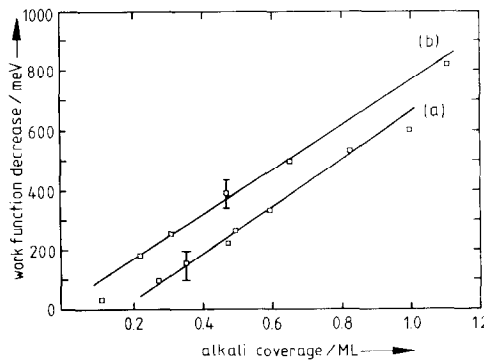


Fig. 2. Work function decrease $\delta\phi_m$ (with respect to the partially alkali covered surface) obtained upon oxygen exposure for various alkali precoverages of W(110): (a) precoverage by Cs, (b) precoverage by Na.

Table 1

Work function decrease $\delta\phi_m$ of alkali covered W(110) subjected to oxygen exposure

Cesium covered W(110)		Sodium covered W(110)	
θ_{Cs} (ML)	$\delta\phi_m$ (meV)	θ_{Na} (ML)	$\delta\phi_m$ (meV)
0.12	30	0.18	153
0.28	50	0.23	179
0.36	148	0.32	251
0.48	221	0.48	389
0.50	257	0.66	496
0.60	331	1.11	818
0.83	529		
1.00	602		

where c is a constant, $\theta_0 = (0.2 \pm 0.03)$ ML and $n = 1$ within the accuracy of the experiment. The absolute values of $\delta\phi_m$ are reproducible with 50 meV as is indicated in fig. 2.

Table 1 gives the values of the work function decrease induced by the oxygen exposure with respect to the values of the various cesium precoverages.

Fig. 3 displays the O(512 eV) AES signal versus oxygen exposure for a full monolayer coverage of Cs. The work function ϕ reaches its minimum at an exposure of 2.2 L (curve denoted by "1 ML" in fig. 1). At this exposure the AES signal has already reached 75% of the saturation value (see arrow in fig. 3). Attenuation of the O(512 eV) AES signal by the alkali overlayer would make this ratio even larger. As was shown in [8] the attenuation of the auger signal amounts to 23% for full monolayer coverage.

The clean W(110) surface shows the expected LEED pattern without extra spots. For Cs coverages larger than 0.64 ML extra spots characterizing a hexagonal structure of the Cs film appear in addition to the normal LEED

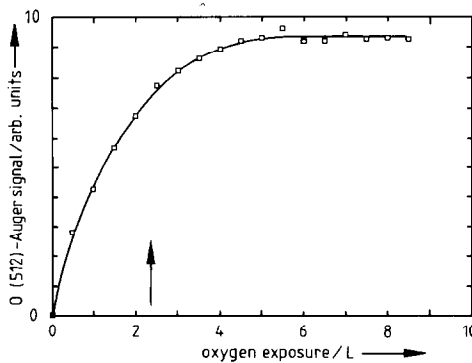


Fig. 3. Variation of the O(512 eV) AES signal upon oxygen exposure for W(110) precovered by 1 ML of Cs.

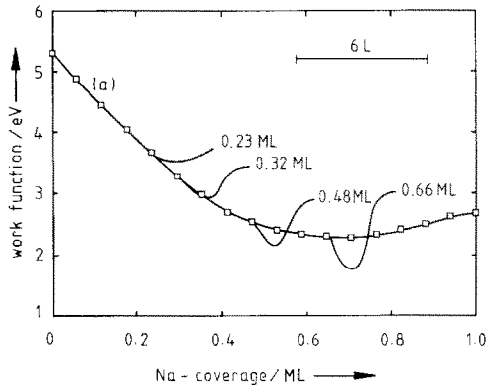


Fig. 4. Variation of the work function of W(110) precovered by Na as a function of the oxygen exposure. See fig. 1 and explanations given in the text.

spots. We observed a stretching of the Cs hexagon in the $[1\bar{1}0]$ direction with a magnitude of about 6%. A similar effect has been found for Cs adsorption on GaAs(110) [11]. For lower coverages only a ring around the (0, 0) reflex rather than spots could be observed at room temperature between 0.3 and 0.64 ML. These observations are in agreement with refs. [6,9].

When a Cs film with a coverage > 0.64 ML is exposed to oxygen, the Cs and W spots become more intense indicating that the mobility of the Cs atoms is reduced. In addition extra spots due to oxygen adsorption appear. All spots except the normal spots due to the substrate disappear rather suddenly as soon as the minimum of the work function is passed (i.e. at oxygen exposures larger than ~ 2 L). For Cs coverages < 0.3 ML only the normal spots can be seen at all oxygen exposures; they grow in intensity when oxygen is offered. Between 0.3 and 0.6 ML Cs coverage weak spots due to oxygen can be observed in addition to the normal spots up to an exposure of 2 L.

For the Na adsorption there is no ordered structure observable up to the largest studied coverage of about 1.5 ML. Oxygen coadsorption does not produce an ordered structure. Fig. 4 shows the variation of the work function of W(110) partially covered by Na when subjected to oxygen adsorption for different initial Na precoverages. The results are presented in the same manner as in fig. 1 for Cs. Fig. 2b shows the magnitude of the work function decrease for the studied Na precoverages. The dependence of the magnitude of the decrease upon the Na precoverage can again be represented by eq. (1). Within the accuracy of the measurements $n = 1$ and $\theta_0 = 0$. For $\theta_{Na} > 0.2$ ML the work function decrease at a given Na coverage is systematically larger (about 100 meV) than the decrease for the same Cs coverage. Table 1 lists as a function of the Na coverage the maximal work function decrease with respect to the value of the Na precoverage.

AES data were not taken for Na covered surfaces under attack of oxygen.

Both for Na and Cs we recognize the following trend between the alkali precoverage and the saturation work function after long oxygen exposures (see figs. 1 and 4): a small (large) decrease of the work function upon oxygen exposure goes together with a small (large) rise from the minimum value up to the saturation value. This increase is roughly three to five times larger than the initial decrease of the work function following oxygen exposure.

4. Interpretation

We will concentrate on the change of the work function upon oxygen exposure of W(110) partially covered by alkali atoms as shown in figs. 1, 2 and 4. For the coadsorption of alkali atoms and oxygen on tungsten our results appear to be the first ones to show the rather clear relationship between the magnitude of the work function decrease on oxygen exposure and the coverage by alkali atoms in the submonolayer range. Such a relationship was however recently reported for the coadsorption of the alkali metals Li, K and Cs and oxygen on Ag(111) [7,8].

In the following we will discuss the work function variations in terms of the model proposed in refs. [7,8] by Rhead and coworkers. They assume:

(1) the Cs layer provides two different sites for adsorption of oxygen atoms called "top" (T) and "under" (U) sites: the adsorption of oxygen on a T-site leads to an increase of the work function while an adsorption at U-sites leads to a decrease of the work function, which is due to the change of the surface dipole moments in both cases,

(2) the binding at the U-sites is stronger than at T-sites so that an U-site remains occupied once it became filled. On the other hand a transfer of oxygen from a T-site to an U-site will occur by surface diffusion as long as unoccupied U-sites are available.

Parker and Rhead [7] could explain their results for Li and oxygen on Ag(111) (described by eq. (1) with $n = 4$) by postulating that the density of U-sites varies as θ_{Li}^4 , where θ_{Li} is the partial coverage by Li. They propose that a U-site in their case results from a random association of four Li-atoms into a surface cluster on the Ag-substrate. With this model they could not only reproduce the θ_{Li}^4 -dependence of the work function decrease $\delta\phi_m$, but also the work function variation with the oxygen exposure over a wide range in a semiquantitative way.

For K and Cs coadsorbed with oxygen on Ag(111) [8] U-sites are only available for alkali precoverages larger than the one corresponding to the work function minimum, θ_m (e.g. 0.6 ± 0.05 ML for K and Cs and Ag(111)). It is found that in this case the initial decrease of ϕ on oxidation, $\delta\phi_m$, is roughly proportional to $(\theta - \theta_m)$.

The LEED results suggest that in our case a rearrangement of the alkali atoms leading to surface clustering is not required to accommodate oxygen atoms at U-sites: the hexagonal LEED pattern seen for Cs coverages larger than 0.64 ML remains visible up to an oxygen exposure of about 2 L. Coadsorption of Na and oxygen does not lead to an ordered structure.

We conclude, that the adsorption of oxygen on U-sites is not structure-induced as in the the case of Li-adsorption on Ag(111), but it is a function of the number of alkali atoms preadsorbed on the surface as soon as U-sites become available. Thus, the number of oxygen atoms which can be accommodated varies linearly with the alkali coverage; this also hold for the work function decrease which results upon oxygen adsorption (see eq. (1)) as long as Helmholtz's equation is valid. This argumentation applies equally for Cs and for Na on W(110). The relation between the alkali coverage θ and $\delta\phi_m$ is of the same form as found for K and Cs coadsorbed with oxygen on Ag(111) [8]. In contrast we find for the coadsorption on W(110) that U-sites are available at coverages smaller than that corresponding to the work function minimum.

A small initial increase of the work function is found for a Cs precoverage larger than 0.64 ML and small oxygen doses (< 0.5 L); in this range extra LEED spots appear due to the oxygen adsorption. Our LEED results suggest that, besides the U- and T-sites, a third possibility for oxygen adsorption exists in this range of coverage which is correlated with the observed stretching of the Cs hexagon as explained above. Because this does not affect the interpretation of our results it will not be discussed any further.

We now discuss the correlation between the alkali coverage and the saturation work function after long oxygen exposures: a small decrease of the work function from its initial value of the partially covered surface goes together with a small rise from $\delta\phi_m$ value to the saturation value. A large decrease due to a large number of unoccupied U-sites gives a large rise. Such a correlation seems not to exist for the adsorption of Li, K, Cs and oxygen on Ag. From our Auger data it can be seen that for 1 ML Cs coverage more than 75% of the saturation coverage of oxygen is already reached at the point the work function reaches the minimum. For all alkali-substrate combinations studied so far (including refs. [7,8]) the work function rise at 1 ML alkali coverage to its saturation value after long oxygen exposures is between 1.2 eV (Na/O-W(110)) and 1.7 eV (Cs/O-W(110)). We may conclude two things:

(1) Because a relatively small additional exposure of oxygen is sufficient to reach saturation at 1 ML precoverage, a structural change may be responsible for the rapid change of the work function ϕ beyond ϕ_m . This is supported by the sudden disappearance of the LEED spots corresponding to the adsorbate (Cs/O-W(110)) when ϕ_m is passed. This interpretation would imply that the rise of ϕ is not simply due to additional oxygen adsorption on top (T-site adsorption [7]) of the alkali layer, but should rather be ascribed to the formation of an alkali-oxygen compound which possesses a smaller dipole

moment than either the pure alkali layer and the compound formed by U-site adsorption.

(2) The weak dependence of the work function rise on the substrate suggests that the same type of alkali-oxygen compound is formed in all cases (for large alkali precoverages) at large oxygen exposures (> 2 L).

In [3] we have scattered Li^+ -ions from cesiated W(110)-surfaces exposed to oxygen. The yield of Li(2p) atoms was drastically enhanced after all U-sites were filled. On the other hand, the Li(2p)-yield remained largely unaffected as long as the oxygen was attached to U-sites. We concluded that after the occupation of U-sites the surface layer is still formed by Cs-atoms; therefore the probability for electron transfer between the Li^+ -projectile and the surface remains largely the same as for the cesiated surface. On the other hand, further oxygen adsorption (> 2 L oxygen) reduces the free-electron state density at the surface drastically because the valence electrons of all Cs atoms are now involved in the binding of the oxygen. Consequently, the probability for electron transfer between the Li^+ -projectile and the surface is drastically reduced. This interpretation finds convincing support in the results of MIES (metastable impact electron spectroscopy) studies carried out on thick cesium layers which were subjected to oxygen exposure [12], and is in good agreement with the results presented here.

5. Summary

We see a relation between the precoverage by alkali atoms of a W(110) surface and the variation of the work function versus the oxygen exposure. The exposure dependence can be explained when supposing two different modes for oxygen adsorption: U-sites are filled first because of their larger binding energy. This leads to an initial decrease of the work function upon oxygen exposure. Here the surface layer is still formed by alkali atoms. The work function starts to increase when all U-sites are filled: the oxygenated alkali surface seems to undergo a structural change. Compared to U-site adsorption the newly formed alkali-oxygen compound possesses a considerably smaller surface dipole moment.

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