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# Cesium-catalyzed oxidation of zinc surfaces

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On zinc films, the adsorption probability of $O_2$ is extremely low ($10^{-3}$–$10^{-2}$), and $O_2$ exposures in the range of $10^3$–$10^4$ langmuir are necessary to produce a significant transformation of metallic zinc into zinc oxide. The presence of submonolayer coverages of cesium enhances the oxidation rate of zinc by 2–3 orders of magnitude. The cesium adatoms interact with $O_2$ molecules, producing a reservoir of reactive oxygen species that oxidize zinc.

**Keywords:** Zn oxidation; Cs catalysis; Cs/ZnO

## 1. Introduction

Zinc oxide has important applications in areas of catalysis, materials science and microelectronics [1,2]. This fact has motivated many studies investigating the synthesis and properties of ultrathin films of zinc oxide. In one type of approach, the $ZnO_x$ films are prepared under a well characterized vacuum environment ($10^{-7}$–$10^{-3}$ Torr base pressure) by direct oxidation of metallic Zn with $O_2$ [3–7]. Films synthesized in this way are directly used in industrial applications, and can serve as model systems to examine the reactivity of the oxide toward metals (Cu, Ni, Pt, etc.) and small molecules ($H_2$, CO, $H_2O$, $CH_3OH$, $C_2H_4$, etc.) present in catalytic processes [2–7].

The heat of formation of zinc oxide is large ($Zn_{solid} + \frac{1}{2}O_{2,gas} \rightarrow ZnO_{solid}$, $\Delta H_f^\circ = -83$ kcal/mol [8]). However, the dissociative chemisorption of dioxygen on zinc surfaces is a kinetically rather slow process (the sticking probability for dissociation being in the order of $10^{-3}$–$10^{-2}$ [5,9]), and large $O_2$ exposures ($10^3$–$10^4$ langmuir [3–7]) are necessary to produce a significant transformation of metallic zinc into zinc oxide. On clean Zn(001), the dissociative adsorption of dioxygen occurs via a thermally-accommodated precursor state: $O_2(\text{gas}) \rightleftharpoons O_2^{\delta-}(\text{surface transient}) \rightarrow 2O^-(\text{chemisorbed}) \rightarrow 2O^{2-}(\text{in bulk})$, that has a very low residence time on the surface [9]. In order to increase the rate of oxidation of zinc, a more efficient source of oxygen must be found.

It is well known that the alkali elements are very reactive toward molecular oxygen. In a few systems [10–13], it has been found that alkali atoms promote the oxidation of the surface on which they are adsorbed. Potassium increases the rate of oxidation of Cu(100) by several (4–6) orders of magnitude [11]. Similarly, sodium raises the oxidation rate of aluminum films by nearly four orders of magnitude [10]. On silicon surfaces, alkali overlayers largely enhance the rate of formation of thin $SiO_x$ films [12,13]. With this in mind, we decided to investigate the effects of cesium on the oxidation of zinc surfaces. We found that the presence of cesium increases the oxidation rate of zinc surfaces by 2–3 orders of magnitude.

## 2. Experimental

The experiments described in section 3 were performed in an ultrahigh vacuum system (base pressure $< 5 \times 10^{-10}$ Torr) equipped with a Mg Kα X-ray source and a hemispherical electron-energy analyzer with multichannel detection. In the photoemission studies, electron detection was perpendicular to the surface, and the X-ray source was at an incident angle of 60° from the surface normal.

Films of zinc were vapor deposited onto a Ru(001) crystal by resistively heating a W filament wrapped with a high-purity wire of zinc. The rate of zinc deposition on the ruthenium substrate was calibrated using thermal desorption mass spectroscopy (TDS) [5]. Zinc is not soluble in Ru(001) [5,15]. The electronic and structural properties of the Zn/Ru(001) systems are examined in refs. [5,15]. Cesium was evaporated onto the zinc films from a carefully outgassed getter chromate source. The rate of cesium deposition was determined by means of TDS [14]. In this work, zinc and cesium coverages are reported with respect to the number of Ru(001) surface atoms ($1.57 \times 10^{15}$ atoms $cm^{-2}$). One adatom per ruthenium surface atom corresponds to $\theta = 1.0$ ML [5,14].

## 3. Results and discussion

A detailed study of the interaction of cesium atoms with zinc films is presented elsewhere [16]. Cesium does not form bulk alloys with zinc [15–17]. At submonolayer coverage of cesium, the very large difference between the surface free energies of cesium (0.067 J $m^{-2}$ [18]) and zinc (0.936 J $m^{-2}$ [18]) prevents the migration of the alkali into the "bulk" of the zinc film [15].

Fig. 1 compares $O_2$ uptakes on clean zinc films and on zinc films partially covered by 0.28 ML of cesium. The experiments were carried out at 300 K, and the amount of adsorbed oxygen was assumed to be proportional to the area measured under the O(1s) features of the XPS spectrum after dosing $O_2$. For thick Zn and Cs/Zn overlayers, diffusion of oxygen into the "bulk" of the film is expected, and the variation in intensity of the O(1s) features with increasing $O_2$ exposure represents a lower limit to the actual change in the amount of adsorbed oxygen. In fig. 1,

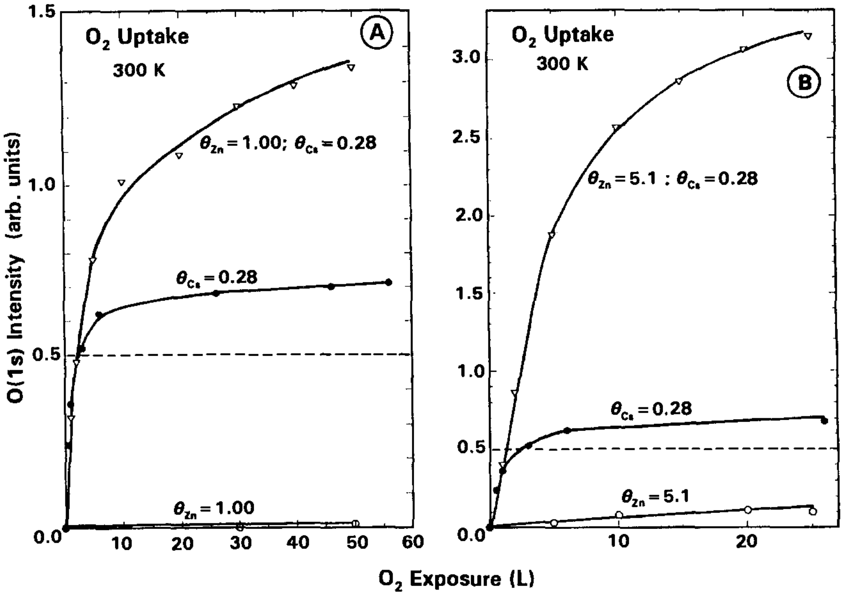

Fig. 1. Variation of the O(1s)-integrated signal with $O_2$ exposure for Zn overlayers on Ru(001) (○), 0.28 ML of Cs on Ru(001) (●), and films containing Zn and Cs (▽). The dashed lines represent the O(1s) intensity measured for 0.5 ML of O on Ru(001). This is the oxygen saturation coverage obtained on Ru(001) after dosing $O_2$ under ultrahigh vacuum conditions at room temperature. 1 langmuir (L) = $10^{-6}$ Torr s.

the dashed lines indicate the O(1s) intensity measured in our instrument for 0.5 ML of O on Ru(001). Previous studies indicate that the bonding between ruthenium and zinc decreases the reactivity of zinc toward $O_2$ [5]. For the supported zinc monolayer, the initial uptake of $O_2$ is much smaller than that for the thick zinc film. It is quire clear that cesium enhances the adsorption rate of $O_2$ on the zinc films. The initial slopes in the curves of fig. 1B indicate that the rate of oxidation of the cesium-promoted zinc film is at least two orders of magnitude faster than that of the clean zinc film. After large exposures of $O_2$, the ratio of the amount of adsorbed oxygen to the amount of cesium present in the film is larger than 10. This is not consistent with the formation of a system that contains only Cs–O bonds. The results in fig. 1 indicate that cesium catalyzes the oxidation of metallic zinc.

Fig. 2 displays O(1s) XPS spectra taken after dosing $O_2$ to a $\{\theta_{Cs} = 0.28$ ML, $\theta_{Zn} = 5.1$ ML$\}$ film at 300 K. The position of the O(1s) peak changes from 529.9 eV at an $O_2$ exposure of 2 L to 530.2 eV at an $O_2$ exposure of 25 L. This range of peak positions matches the values reported for ZnO (530.0–530.5 eV [19]) and $Cs_2O_2$ (530–531 eV [20]). The results in fig. 2 indicate the absence of $Cs_2O$ (which is characterized by an O(1s) peak from 526.0 to 527.6 eV [20]) and $CsO_2$ (which is characterized by an O(1s) peak at 533.7 eV [20]) on the oxidized film. In general, we found that $Cs_2O_2$ and $ZnO_x$ were the only oxides produced during the oxidation of Cs/Zn films at 300 K.

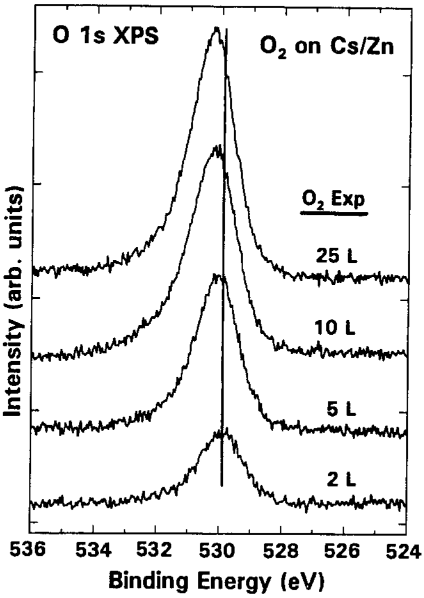

Fig. 2. O(1s) XPS spectra taken after dosing 2, 5, 10 and 25 L of $O_2$ to a film containing 5.1 ML of Zn and 0.28 ML of Cs. The experiments were carried out at 300 K.

Fig. 3 shows Cs(3d) XPS spectra acquired before and after exposing a $\{\theta_{Cs} = 0.28$ ML, $\theta_{Zn} = 5.1$ ML$\}$ film to $O_2$ at 300 K. An $O_2$ dose of 2 L leads to an increase in the intensity of the Cs $3d_{5/2}$ peak and shifts the peak position by $\sim -0.5$ eV. This behavior is consistent with the formation of $Cs_2O_2$ [20]. An increase in $O_2$ exposure from 2 to 20 L does not produce any significant change in

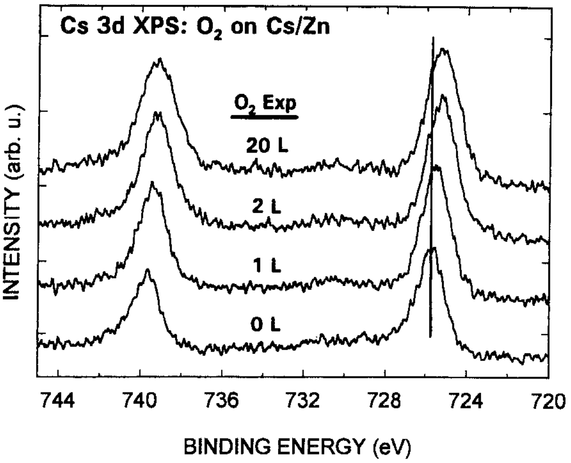

Fig. 3. Cs(3d) XPS spectra acquired before and after oxidizing a film containing 5.1 ML of Zn and 0.28 ML of Cs. Oxygen was dosed at 300 K.

the Cs $3d_{5/2}$ peak position, suggesting that a complete transformation of Cs into $Cs_2O_2$ has already occurred at an $O_2$ exposure of 2 L. After "saturating" the Cs adatoms, the additional oxygen that is adsorbed reacts with Zn. In fig. 3, the lack of attenuation of the Cs(3d) XPS signal with $O_2$ exposure indicates that the cesium cations remain on top of the oxidized film.

The Zn $L_3M_{45}M_{45}$ Auger transition is very sensitive to the formation of bonds between zinc and oxygen [19b,21,22]. Fig. 4 shows Zn $L_3M_{45}M_{45}$ Auger spectra acquired before and after dosing 50 L of $O_2$ to a $\{\theta_{Cs} = 0.28$ ML, $\theta_{Zn} = 5.1$ ML$\}$ film at 300 K. The change in the line-shape of the Auger features and the shift of ~ 4 eV toward lower kinetic energy are characteristic of the formation of zinc oxide [19b,22]. After an $O_2$ exposure of only 50 L most of the metallic Zn has been transformed into $ZnO_x$. To obtain similar changes for a zinc film without cesium, one needs an $O_2$ exposure larger than $10^4$ L [5]. The Zn $L_3M_{45}M_{45}$ Auger spectra for the $\{\theta_{Cs} = 0.28$ ML, $\theta_{Zn} = 1.00$ ML$\}$ film in fig. 1A showed a complete oxidation of zinc after an $O_2$ exposure of 50 L. In contrast, the corresponding Auger spectra for a Zn monolayer exposed to 6000 L of $O_2$ (see fig. 6 in ref. [5]) showed that more than 50% of the zinc was still metallic.

For the oxidation of the cesium-promoted zinc surfaces, we propose the reaction scheme displayed in fig. 5. During the oxidation of a clean zinc surface, the key intermediate is a weakly adsorbed $O_2^{\delta-}$ species that exhibits a very low probability for dissociation into atomic oxygen [9]. For the cesium-promoted surface, an attractive interaction between the $O_2^{\delta-}$ species and a $Cs^{\delta+}$ cation probably increases

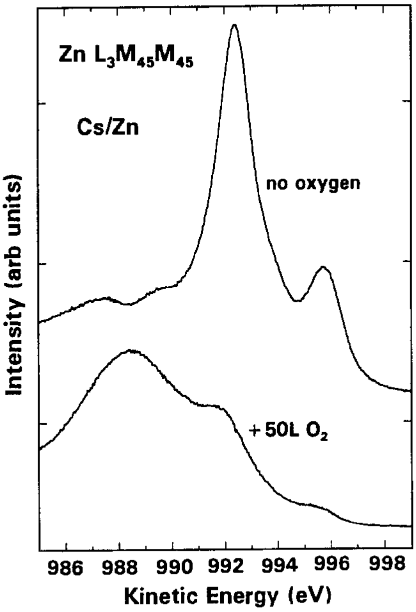

Fig. 4. Zn $L_3M_{45}M_{45}$ Auger spectra acquired before and after dosing 50 L of $O_2$ to a film containing 5.1 ML of Zn and 0.28 ML of Cs. The experiments were performed at 300 K.

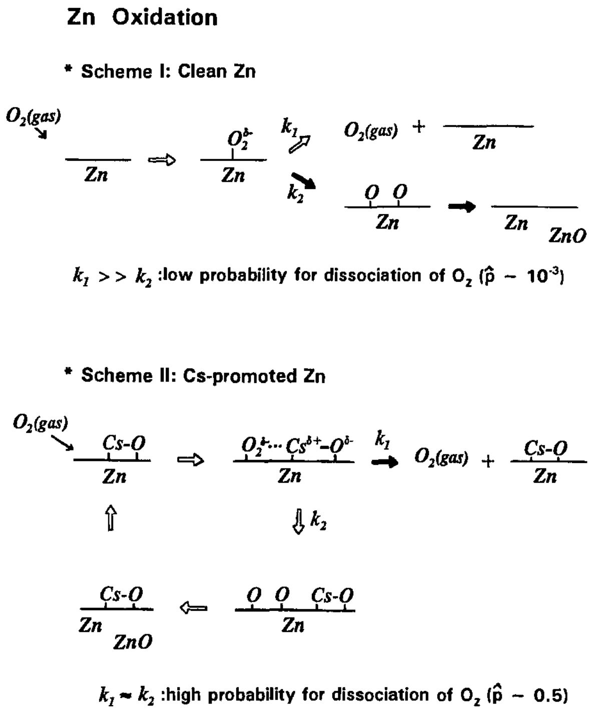

Fig. 5. Reaction schemes for the oxidation of clean and Cs-promoted Zn surfaces.

the residence time of the $O_2^{\delta-}$ species on the surface, favoring its dissociation into atomic oxygen that rapidly moves into the "bulk" of the zinc film.

The results presented in this communication show that cesium is an effective catalyst for the oxidation of zinc surfaces. This catalytic effect should be particularly useful for the synthesis of $ZnO_x$ films under ultrahigh vacuum conditions. Once that the $ZnO_x$ film has been prepared, the small amount of cesium that is necessary to produce a catalytic effect can be removed from the surface of the oxide by annealing to high temperature (800–900 K) and/or ion sputtering. In some cases, it may not be necessary to remove the cesium from the zinc oxide film. It is well known that cesium is a promoter for the water–gas shift and methanol synthesis reactions over Cu/ZnO catalysts [23,24]. Thus, in the preparation of model Cs/ZnO and Cs/Cu/ZnO catalysts the presence of cesium could be an advantage instead of a problem.

## 4. Conclusions

The presence of cesium enhances the oxidation rate of zinc films ($O_{2,gas} + Zn_{solid} \rightarrow ZnO_{solid}$) by 2–3 orders of magnitude at room temperature. The cesium adatoms interact with $O_2$ molecules, producing a reservoir of oxygen species that react with zinc.

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