

LETTER TO THE EDITOR

Oxygen Dimerization at a Zn(0001)–O Surface

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The presence of Ba at a Zn(0001)–O surface (up to $\theta_{\text{Ba}} \sim 3$ ML) gives rise to BaO, followed by a peroxo-type species (Ba, Zn) $\text{O}_2^{\delta-}$ at the interface. Such peroxo species are also formed when a Ba-covered Zn surface ($\theta_{\text{Ba}} \sim 0.3$ ML) exposed to dioxygen at 200 K is warmed to 400 K. Peroxo formation occurs via the oxidation of O^{2-} species. © 1994 Academic Press, Inc.

It has been shown by Carley *et al.* (1) that a small coverage of Ba ($\theta_{\text{Ba}} \sim 0.1$ ML) on a Zn(0001) surface increases the rate of cleavage of the dioxygen bond, giving rise to a dramatic increase in the rate of formation of the oxide species O^{2-} (a) at the surface. It has been proposed that a mobile $\text{O}_2^{\delta-}$ species is involved in this process. A detailed study of the interaction of oxygen with Ba-covered Zn(0001) surfaces (2) has clearly shown the formation of peroxo species as well as oxidic species, depending on the Ba coverage and oxygen exposure. As a sequel to this study, we have studied the effect of deposition of Ba on ZnO (grown on a Zn(0001) surface by *in situ* oxidation at 400 K). This study has indeed revealed the formation of a novel peroxo species, also found when an oxygen-exposed Zn(0001)–Ba surface ($\theta_{\text{Ba}} \sim 0.3$ ML) is warmed from 200 to 400 K.

A freshly cleaved Zn(0001) crystal was mounted in the ESCA3 spectrometer, cleaned by argon ion bombardment, and annealed at 150°C. Surface cleanliness was checked by XPS and LEED, the latter giving a sharp hexagonal pattern corresponding to the (0001) face. Oxidation of Zn was performed at 400 K (oxygen exposure = 10,000 L; 1 L $\equiv 10^{-6}$ Torr·sec), and Ba was dosed on the oxide surface at 295 K. The binding energies are referred to the $\text{Zn}2p_{3/2}$ level (1021.6 eV). Data acquisition was performed using commercial software (SPECTRA) and analyzed using software developed in house (3).

In Fig. 1 we show the effect of depositing Ba on the ZnO surface on both the O(1s) and the Zn($L_3M_{45}M_{45}$) spectra. For a Ba coverage of 2.5 ML we observe (Fig. 1) a shift in the O1s peak at 530 eV, which is characteristic

(2) of ZnO, to a lower binding energy of 529 eV, which we ascribe (2) to the formation of BaO. More interestingly, we see a feature at 532 eV which we assign to a peroxo-type species, (Ba, Zn) $\text{O}_2^{\delta-}$, which is similar to that formed on exposing Ba-covered Zn surface to oxygen (2) and different from BaO_2 . Increasing the Ba coverage to 3.2 ML leads to an increase in intensity of this 532-eV feature. In Fig. 2 we show the decomposition of the observed O(1s) band into peaks associated with the three different types of oxygen species associated with BaO, ZnO, and (Ba, Zn) $\text{O}_2^{\delta-}$. Accompanying the progressive formation of the peroxo-type species, we see the reduction of ZnO, as

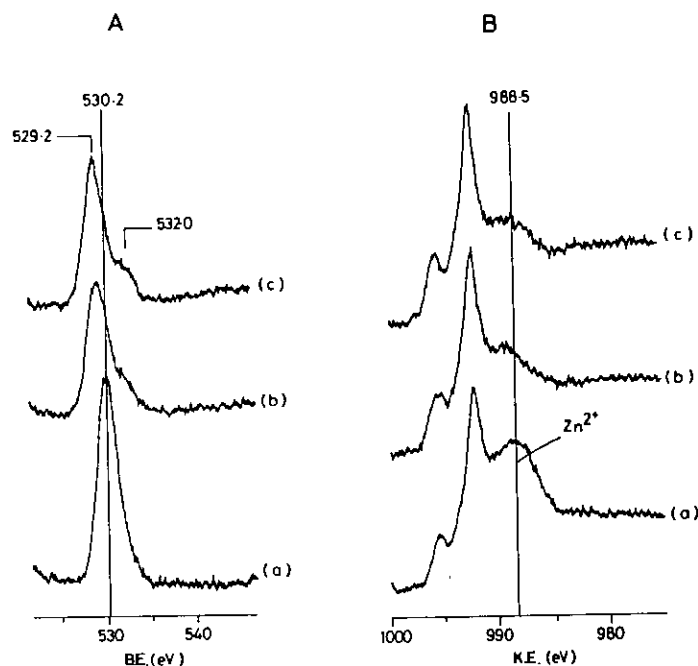


FIG. 1. (A) O(1s) spectra and (B) Zn($L_3M_{45}M_{45}$) spectra showing the effect of Ba deposition on an oxide overlayer on Zn(0001). (a) ZnO overlayer ($\sigma_0 = 2.0 \times 10^{15}$ cm $^{-2}$); (b) after depositing 2.5 ML barium; (c) after depositing 3.2 ML barium.

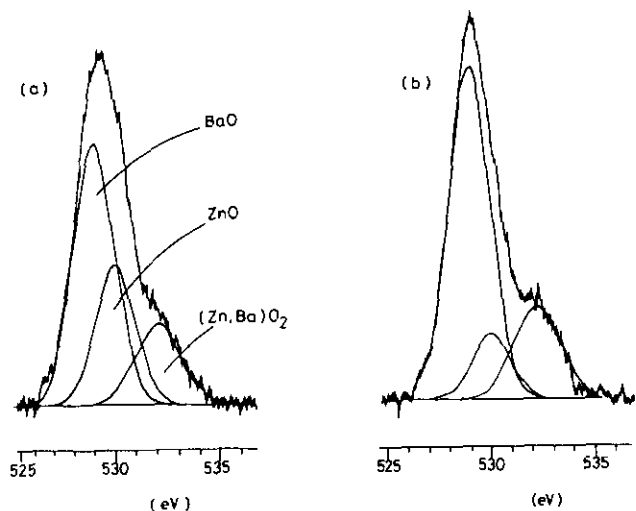
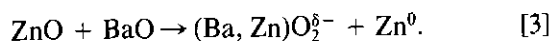
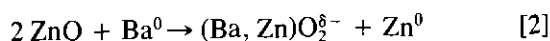
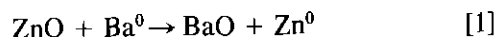
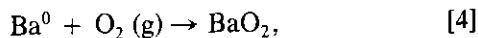


FIG. 2. O(1s) spectra from Fig. 1, curve fitted to the three components identified at the Ba-modified Zn(0001) surface: (a) $\theta_{\text{Ba}} = 2.5$ ML; (b) $\theta_{\text{Ba}} = 3.2$ ML.

evidenced by a decrease in the intensity of the Zn($L_3M_{45}M_{45}$) Auger line at 988.5 eV characteristic of Zn²⁺ (Fig. 1). The transformations are described by the following equations:



The peroxo species must be of the type $(\text{Ba, Zn})\text{O}_2^{\delta-}$ formed by reaction [2] and/or [3], rather than BaO_2 resulting from the direct interaction of Ba metal with oxygen,



since BaO_2 is associated with a characteristic O(1s) feature (2) at 531 eV.

In Fig. 3 we show a schematic representation of the processes occurring during the deposition of Ba on a ZnO overlayer on Zn(0001).

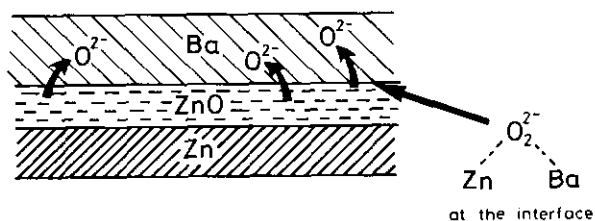


FIG. 3. A schematic representation of the processes occurring during the deposition of Ba on a ZnO overlayer on Zn(0001).

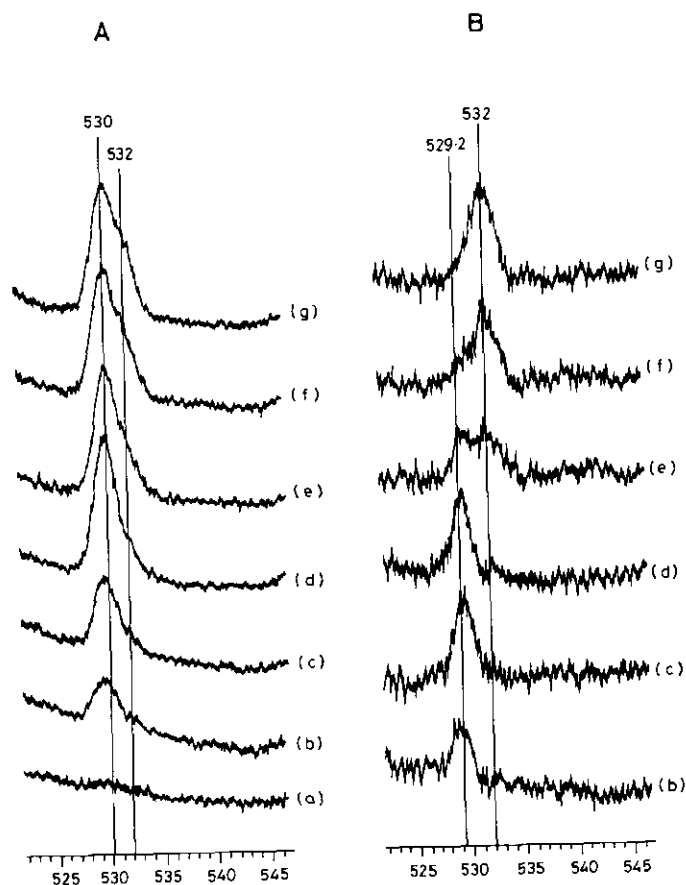


FIG. 4. (A) O(1s) spectra for a Zn(0001) surface doped with barium at 300 K ($\theta_{\text{Ba}} = 0.3$ ML) and then exposed to dioxygen at 200 K: (a) Zn(0001)-Ba, (b) 0.5 L, (c) 1 L, (d) 5 L. Warming then occurred in stages: (e) 220, (f) 300, (g) 400 K. (B) O(1s) difference spectra (after subtracting the O(1s) contribution due to ZnO from the O(1s) raw spectra) corresponding to spectra (b)-(g) in (A).

surface. On deposition of Ba, oxide ions diffuse out into the Ba overlayer to form BaO. Evidence for such outward diffusion of the oxide ions has been obtained from a comparison of the attenuation of the O(1s) and Zn($2p_{3/2}$) intensities by the barium overlayer. While the Zn($2p_{3/2}$) peak intensity is attenuated by 75%, that of the O(1s) signal is reduced by only 23%, clearly indicating that the O²⁻ ions have migrated toward the barium-vacuum interface. In contrast, the $(\text{Ba, Zn})\text{O}_2^{\delta-}$ -type peroxo species is likely to be formed at the Ba-ZnO interface.

We have obtained evidence for the mechanism of formation of the $(\text{Ba, Zn})\text{O}_2^{\delta-}$ peroxo species from a variable-temperature study of an oxygen-exposed Ba-modified Zn surface. In Fig. 4, we show the O(1s) spectra of a Zn(0001)-Ba surface ($\theta_{\text{Ba}} = 0.3$ ML) exposed to oxygen at 200 K. For low exposures of oxygen (0.5 L), the O(1s) peak appears at 529.2 eV but shifts to 530 eV with further oxygen exposure, reflecting the initial formation of Ba-O-type species (529.2-eV peak), followed at higher oxygen

exposures (5 L) by Zn-O species (530-eV feature). This ZnO component has been subtracted from the raw O(1s) spectra, using an O(1s) spectrum measured after oxidation of an undoped Zn(0001) surface, to generate the difference spectra shown in Fig. 4. On increasing the temperature of the adlayer in stages from 200 to 400 K, a feature at 532 eV gradually emerges, due to the formation of (Ba, Zn)O₂^{δ-}-type peroxo species. The increase in intensity of the 532-eV feature is accompanied by a decrease in the intensity of the O1s feature at 529 eV due to BaO. It therefore appears that the peroxo species results from the interaction of BaO with ZnO according to reaction [3] rather than reaction [2]. This is corroborated by the observed increase in intensity of the O(1s) difference spectrum by a factor close to 2 as the surface is warmed from 200 to 400 K, the "extra" oxygens originating from ZnO species.

The dimerization of O²⁻ to form O₂²⁻ is likely to proceed

according to $2O^{2-} \rightarrow 2O^{1-} \rightarrow O_2^{2-}$, a sequence of steps involving the oxidation of oxide ions, which is the exact opposite of that encountered in the formation of oxide ions on surfaces (4), involving the reduction of O₂. The observation of such a dimerization reaction is noteworthy.

ACKNOWLEDGMENT

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