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Interaction of oxygen with polycrystalline cobalt studied by inverse-photoemission spectroscopy

Lamberto Duò, Marco Finazzi, Franco Ciccacci, and Lucio Braicovich
Dipartimento di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy

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We report a room-temperature UV inverse-photoemission study of the early oxidation stages of polycrystalline cobalt within the photon energy range 12–25 eV for exposures between 1 and 10^4 Langmuir (L) (1 L$=10^{-6}$ Torr s). The decomposition of each spectrum related to intermediate exposures in terms of bulk Co and oxidized Co, together with the analysis of the relative intensities for the different contributions, shows the stable formation of CoO at the interface for exposures ≥ 30 L, whereas for lower exposures the oxide stoichiometry depends on the amount of oxygen atoms. In the 5–7-L range, possible Co_3O_4 formation takes place consistently with a decreased interdiffusion in this regime as compared to the higher exposures regime. An estimation of the oxide film thickness at the maximum exposure is performed giving a surface oxide thickness of about 20 Å.

INTRODUCTION

For a long time the oxidation process of clean metal surfaces has been widely recognized to play an essential role in surface chemical reactions, even in connection with topics such as heterogeneous catalysis and corrosion.[1] While many results have been accumulated concerning the evolution of the occupied electronic states (i.e., valence states and core levels) upon oxidation for late transition-metal (TM)/O_2 systems, less attention has been dedicated to the modification experienced by the empty states.[2–8] At present there is no knowledge about the effect on the Co empty *d* states regarding the interaction of O_2 atoms with metallic Co. Such a study is now particularly interesting because of the recent bremsstrahlung-isochromat-spectroscopy (BIS) results on stoichiometric CoO and Co_3O_4 (Ref. 9), which can be used as a helpful reference for a comparison with the spectra of oxidized Co at different oxidation stages.

In this work we perform an inverse-photoemission-spectroscopy (IPES) study of polycrystalline Co oxidation at room temperature in the exposure (θ) range from 1 to 10^4 L (1 L$=10^{-6}$ Torr s) and in the photon energy range 12–25 eV. The results indicate the formation of CoO for oxygen exposures of 30 L and higher, and possible Co_3O_4 formation in the exposure regime 5–7 L. An oxide thickness of about 20 Å is estimated in the 10^4-L case.

EXPERIMENT

High-purity (99.99%) polycrystalline Co was mechanically scraped *in situ* with a diamond file. The equipment is described in detail in Ref. 10. The base pressure during the data collection was $\approx 2\times10^{-10}$ Torr. During the scraping the pressure into the preparation chamber was $\leq 4\times10^{-10}$ Torr. Exposures to oxygen were performed by introducing research-grade oxygen through a leak valve at a pressure between 1×10^{-7} Torr (for $\theta=1$ L) and 2×10^{-5} Torr (for $\theta=10^4$ L) according to the amount of O_2 exposure. All the reported exposures were performed at room temperature onto a freshly cleaned Co surface.

The inverse-photoemission (IPE) spectrograph is based on an ultraviolet grating dispersing photons with energy $h\nu$ in the 10–25-eV range. Spectra have been collected by scanning the electron energy (isochromat mode). The total resolution corresponds to a full width at half maximum (FWHM) between 0.4 eV ($h\nu=12$ eV) and 0.9 eV ($h\nu=24$ eV). The spectra were normalized on line to the impinging current. In order to avoid sample contamination or damaging and charging effects the current density on the sample was kept below $\approx 100\ \mu A/cm^2$.

RESULTS AND DISCUSSION

In Fig. 1 a selection of IPE spectra is shown for a Co surface interacting with increasing oxygen exposures from pure Co up to 10^4 L. The progressive decrease of the relative intensity of the metallic feature—with *d*-like character[11]—upon oxidation is combined with the growth of a new higher-energy structure already visible at an exposure of 17 L at about 2.6 eV above E_F and which becomes clearer from 30 L on at a constant energy about 3.4 eV above E_F. In the case of $\theta=10^4$ L the signal from the metallic feature is not detectable anymore and only the latter structure is seen. The oxidelike feature has a strong *d* character since the *d* cross section is dominant in our $h\nu$ range; this feature is present for all the measured isochromats (not shown here for space reasons).

The energy separation between the two components appearing in Fig. 1 is large enough to allow the determination of their relative weights. Therefore each spectrum of oxidized Co has been decomposed in two different contributions: the first, closer to the Fermi level, derived from the substrate metallic peak and the second representing the effect of the oxidation reaction. While for exposures ≥ 30 L this procedure results in the same oxygen-derived line shape, which in turn is the same as the saturated line shape, as shown in Fig. 2(a), this is not the case for exposures lower than 30 L, where the

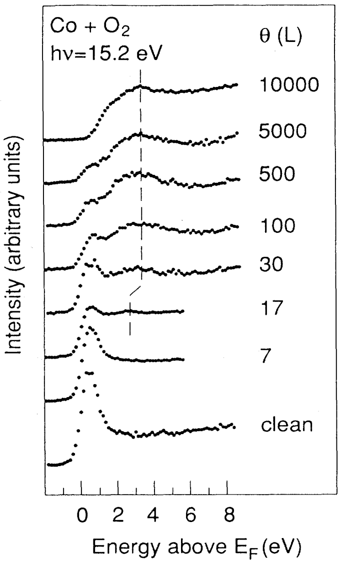

FIG. 1. Selection of IPE spectra at $h\nu = 15.2$ eV for $Co + O_2$ at different exposures. The dashed line shows the peaks forming upon oxidation. At $\theta = 17$ L the peak position is about 2.6 eV while for higher exposures the peak is always found at about 3.4 eV.

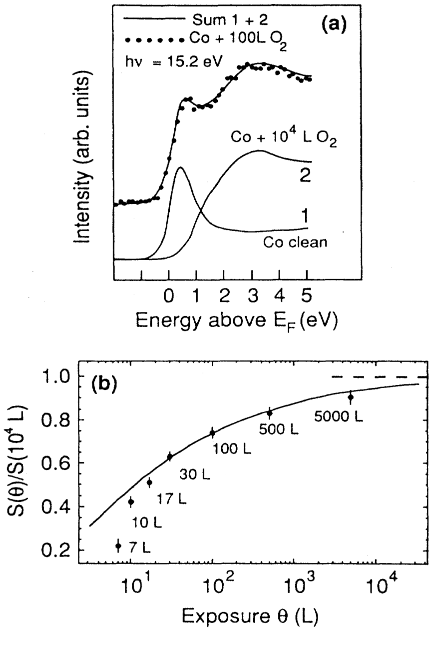

FIG. 2. (a) Example of the decomposition procedure on the oxidized IPES spectra at $h\nu = 15.2$ eV. The $\theta = 100$-L spectrum is fitted with a linear combination of the substrate Co (Co clean) and the saturated Co ($Co + 10^4$ L O_2). (b) Experimental results (dots with error bars) of the ratio $R(\theta) = S(\theta)/S(10^4 \text{ L})$ between the oxide signal intensity for an exposure θ and the saturated oxide intensity (see text). The fitting curve (solid line), according to Eq. (1), is based on the points with $\theta \geq 30$ L. In the right-hand side of the figure the asymptotic $R = 1$ value is also shown.

oxygen-derived profiles do show a dependence on the O_2 exposure. Thus a transition in the interface growth for θ around 30 L, consistently with the x-ray-photoemission spectroscopy (XPS) results of Ref. 12 on poly Co/O_2, is found. These results agree well with the following quantitative analysis of the oxygen uptake on the Co surface.

The experimental intensity ratio $R(\theta) = S/S_\infty$ of the oxygen-induced signal S to the total saturated signal S_∞ has been evaluated versus exposure. These data have been fitted with a theoretical growth model[13] according to which the ratio R varies with the exposure θ in the following way:

$$R(\theta) = 1 - (1 + \theta/\theta_0)^{-\beta} , \qquad (1)$$

where θ_0 and β are parameters depending on the oxidation conditions.[14]

In Fig. 2(b), together with the experimental results (dots with error bars), we give the result of the fitting with the model of Eq. (1). According to this model the point at saturation is at infinite exposure; the experimental data at 10^4-L exposure already give saturation within our sensitivity.

The important result is that it is not possible to fit all measured points with the above-mentioned model. By taking into account all points the resulting χ^2 is 1.97×10^{-2} (with $\theta_0 = 4.78$ L and $\beta = 0.43$), i.e., much worse than the fit obtained with $\theta \geq 30$ L [displayed as a solid line in Fig. 2(b)], which gives $\chi^2 = 2.46 \times 10^{-3}$ (with $\theta_0 = 1.35$ L and $\beta = 0.31$).

In general this model can work only if the oxidation products do not change for different exposure regimes because the experimentally determined parameters, i.e., β and θ_0, are sensitive to the stoichiometry. Since the decomposition procedure shown in Fig. 2(a) gives the same oxygen-induced line shape only for $\theta \geq 30$ L, a good agreement between the model and the experimental results is not to be expected below this exposure, as shown by Fig. 2(b).

In the central panel of Fig. 3 the oxygen-induced line shapes (with $h\nu = 15.2$ eV) are given for $\theta = 7$ and 17 L, and the total profile at $\theta = 10^4$ L. In the upper and lower panels of Fig. 3 the oxygen-induced spectra at $\theta = 7$ and 10^4 L are compared with published BIS results on stoichiometric CoO and Co_3O_4 (Ref. 9).[15] In order to make the energy scale meaningful all the spectra of Fig. 3 have been displayed relative to the conduction-band minimum (CBM) because of the insulating character of the samples.[16] A similar analysis (not shown here) has been performed for $\theta = 5$ and 10 L. For the oxygen-induced profile at 5-L O_2 the results are very similar to that of 7 L while the 10-L profile can be placed in between the cases of 7 and 17 L. Below 5 L, due to the small oxidizedlike signal relative to the Co bulk signal, we do not discuss the results of such an analysis.

The lower panel of Fig. 3 indicates a close resemblance between the $\theta = 10^4$-L and the CoO BIS line shapes strongly suggesting the formation of a stoichiometric CoO compound on top of the Co surface as final product of the oxidation process.[17] Analogously CoO formation at saturation has been found from the photoemission-spectroscopy (PES) results reported in Ref. 18 for the oxi-

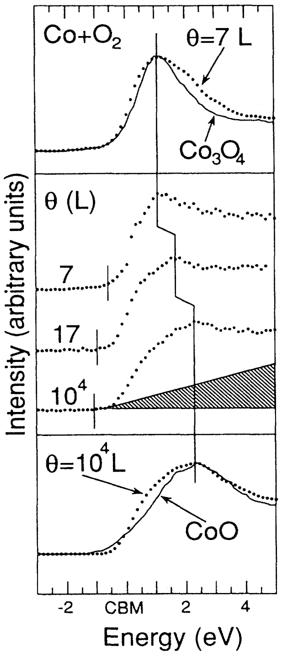

FIG. 3. Comparison between the oxidation-related IPES spectra (dots) ($h\nu = 15.2$ eV) as determined in (a) and bulk Co-oxide spectra (line) from Ref. 9 ($h\nu = 1486.6$ eV) relative to the conduction-band minimum (CBM). Central panel: $\theta = 7$ L; E_F at -0.6 eV and peak at 1.1 eV; $\theta = 17$ L, E_F at -0.9 eV and peak at 1.7 eV; $\theta = 10^4$ L, E_F at -1.1 eV and peak at 2.3 eV. The vertical bars indicate the E_F positions. Upper and lower panels: Both the dotted spectra have been obtained by the two spectra in the central panel after (i) a Gaussian broadening (FWHM=0.5 eV) to simulate the same experimental resolution as in the BIS profiles, and (ii) a linear background subtraction (dashed area below the $\theta = 10^4$-L spectrum; see Ref. 15). For the bulk spectra: CoO with E_F at about -1.7 eV and peak at about 2.3 eV; Co$_3$O$_4$ with E_F at about -1.2 eV and peak at about 1.1 eV (Ref. 9).

dation of polycrystalline Co. From this point of view the present analysis extends those results showing that CoO formation takes place already at exposures as low as 30 L. As shown in Fig. 3 in the θ range 5–7 L the decomposed oxidized line shapes appear very similar to the bulk Co$_3$O$_4$ BIS profile suggesting the formation of Co$_3$O$_4$. This guess is reinforced by Fig. 2(b) clearly showing that the experimental $R(\theta)$ values are considerably smaller in this range than what is expected according to the model working at high exposures. This implies a higher oxygen concentration at the interface, which could reasonably result in an oxygen-rich Co-oxide formation despite the low integral amount of oxygen atoms.

An estimation of the average oxide thickness at saturation can be achieved by relying upon the attenuation of the substrate 3d signal and the fitting parameters obtained from Eq. (1). By assuming a penetration depth λ of 7 Å, which is typical of the metals, in the kinetic-energy range of interest[19] and by considering the geometry of our apparatus a saturation thickness around 15 Å is found. This should be regarded as a lower limit because in the oxides the presence of an energy gap makes λ larger than in the metals by about 60–70%.[19] This results in an upper-limit estimation of the oxide thickness around 25 Å. The average oxide thickness at saturation evaluated here for polycrystalline Co is roughly two times higher than that estimated at saturation exposure at room temperature of hcp(0001) Co by UV PES and Auger spectroscopy.[20] This might suggest that the reaction goes faster in polycrystalline Co.

In conclusion, we have presented a room-temperature inverse-photoemission study of polycrystalline Co oxidation in the θ range $1-10^4$ L. The spectra have been collected, with variable photon energy, in the ultraviolet-energy range between 12 and 25 eV. For $\theta \geq 30$ L the decomposition of each spectrum in terms of an unreacted Co bulk contribution and a surface oxidized component allows one to determine the formation of a stoichiometric or nearly stoichiometric CoO phase at the interface. The thickness of this oxide film increases with θ according to a logarithmic growth, eventually reaching an estimated thickness of about 20 Å at saturation. For lower exposures the growth rate shows deviations from the logarithmic trend of the high-θ regime. The oxidation-related profiles are still evolving and for $\theta = 5-7$ L they strongly resemble the Co$_3$O$_4$ line shape, possibly suggesting an oxygen-rich oxide formation consistent with the very small Co-O interdiffusion in this exposure range.

ACKNOWLEDGMENTS

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[1] See, e.g., the extensive review by C. R. Brundle and J. Q. Broughton, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis,* edited by D. A. King and P. D. Woodruff (Elsevier, Amsterdam, 1990), Vol. 3A, p. 131.

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[14] This model has already been applied successfully in an IPES study of poly Ni/O_2 (Ref. 2) in a similar exposure range.

[15] Due to the higher background in the UV regime compared to the x-ray regime, a background has been subtracted from our spectra (dashed area in Fig. 3) to obtain the same peak-to-background ratio for both the UV and the x-ray results. This is done only to allow a quick comparison between the two sets of spectra and it is not essential, as shown by the raw data (central panel in Fig. 3); the background shape is not relevant here.

[16] The CBM energy has been evaluated starting from the experimentally determined Fermi-level energies and applying the criterion used in Ref. 9, i.e., taking the energy of the point corresponding to 10% intensity of the peak and adding an energy equal to half the FWHM, which is 0.3 eV for our oxidized spectra and 0.4 eV in the case of CoO and Co_3O_4.

[17] Small discrepancies close to the CBM between the two spectra are not relevant here and could be tentatively attributed to the presence of weakly bound oxygen on top of the CoO layers in the oxidation case, consistent with previous results on Co oxidation (Ref. 12).

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