

Oxidation of cadmium: An ultraviolet-photoemission and electron-energy-loss investigation

L. Braicovich and G. Rossi

Istituto di Fisica del Politecnico, 20133 Milano, Italy

R. A. Powell* and W. E. Spicer

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

(Received 10 December 1979)

The first results on the oxidation of metallic Cd performed using the surface-spectroscopic techniques of ultraviolet photoemission (UPS) and electron-energy loss (EELS) are reported. The valence-band UPS spectra of CdO are given for the first time. Both UPS and EELS indicate a clear transition from a chemisorption regime (≤ 2000 Langmuirs) to an oxide regime. In UPS, the $2p$ resonance due to isolated oxygen adatoms is clearly seen at ≈ 3.5 eV below the Fermi level. At increasing oxygen exposure, the $2p$ line shape becomes increasingly asymmetric, and a satellite structure appears at higher binding energy. The fingerprint of the oxide at the surface is the reduction of binding energy of this satellite, which we attribute to a narrowing of the total valence-band width of the Cd-O system as the cubic coordination of the oxide is attained. The EELS results support the general trends observed using UPS. In addition, new insight into loss structure previously observed in CdO at 23 eV is given.

I. INTRODUCTION

The study of the oxidation of group-IIA and -IIB metals with the methods of electron spectroscopy is receiving increasing attention for a variety of reasons. The problem is interesting not only *per se* but in connection with general problems of the metal-oxygen interaction. In addition, the oxides of these metals very often have interesting catalytic properties. Among group-IIB metals, the Zn oxidation problem has been studied in some detail with the methods of electron spectroscopy¹⁻⁴ while, to the authors' knowledge, such studies have not been reported on Cd oxidation. There is, however, a need for information on the oxidation of Cd since this case can by no means be regarded as an obvious extension of the Zn case. Although Cd and Zn are similar metals having the same structure (hcp), CdO and ZnO have quite different structures (rocksalt and wurtzite, respectively). It is thus expected that the oxidation of Zn and Cd have common features only at low exposures where the behavior is determined basically by the interaction of isolated (or nearly isolated) oxygen atoms with the metal, while strong differences between the two cases are expected when the oxide is formed. The present work covers a wide enough range of oxygen exposures so that information on both these regimes and on the transition from one to the other can be obtained. The analogy between the oxidation of Zn and Cd at low exposure is pointed out, although important differences are seen; this also allows us to discuss some problems connected with the oxidation of Zn. At higher exposures, the behavior is peculiar to Cd and is discussed in detail.

These studies have been carried out using the methods of ultraviolet-photoemission spectroscopy (UPS) and of electron-energy-loss spectroscopy (EELS). The combined use of these techniques allowed us to establish, with great confidence, some relevant features of the Cd oxidation. This approach has some methodological value as well, since using both UPS and EELS to study the same system (Cd+O₂) under comparable conditions allows one to compare the two techniques for studies of this kind. Finally, we mention two by-products of the present research: New assignments for structure in the EELS spectrum of CdO are given and the valence-band photoemission spectra of CdO are presented for the first time.

II. EXPERIMENTAL

The photoemission and the electron-energy-loss measurements were performed using separate instruments. The photoelectron-energy-distribution curves (EDC's) were measured with a spherical-grid retarding-potential spectrometer which integrates over an angle of $\approx 2\pi$ sr. He I light ($h\nu = 21.2$ eV) has been used from a dc discharge lamp with windowless differentially pumped coupling to the UHV chamber (base pressure $\approx 1 \times 10^{-10}$ Torr); the light was incident normally onto the sample surface. The total energy resolution of the system was ≈ 0.2 eV. A typical value of the photocurrent was 10^{-12} A, and no evidence was found for perturbation of the adsorption process at these intensity levels.

The EELS measurements were carried out in a UHV chamber (pressure in the upper- 10^{-10} -Torr range) equipped with a single-pass cylindrical

mirror analyzer with a coaxial electron gun, having a fractional energy resolution of $\Delta E/E \approx 0.25\%$. The angle of incidence of the electrons was 30° to the sample normal. Since electron bombardment has been seen to have some influence on oxygen uptake, great care was taken to minimize this effect by reducing the incident current and by defocusing the beam to the maximum spatial size compatible with the loss of energy resolution. For the conditions used in the present experiment, no modification of the EELS spectra has been seen during the first 10 min of exposure to the electron beam; each measurement reported here has been taken in 90 sec, immediately following the oxygen exposure. This point is important since electron-induced adsorption-desorption processes are known to take place in the related compounds CdS and ZnO⁵.

In order to increase the surface sensitivity in EELS measurements, the lowest electron energy allowed by the instrument (150 eV) was used. Besides the $N(E)$ spectra, the dN/dE spectra were also measured with standard modulation techniques.

Samples were cut from a high-purity (99.999%) polycrystalline Cd rod. In the energy-loss experiment, the sample was cleaned by argon bombardment (3-keV energy). In the photoemission experiment, the sample was cleaned *in situ* by mechanical scraping in order to avoid any Cd contamination of the apparatus due to Cd sputtering. *In situ* Auger analysis did not show the presence of contaminants on samples prepared by either of the above methods.

In these experiments, high-purity oxygen was admitted into the chamber through a leak valve and the pressure was measured with a Bayard-Alpert gauge not seen by the sample. The effect of exposures was the same with the gauge on and with the gauge off, so that no evidence was found of artifacts due to excited oxygen. The pressure gauges in the two apparatus were not calibrated so that there might be a mismatch between the two exposure scales of up to a factor of ≈ 2 . Oxygen exposures have been made at 2×10^{-6} Torr for exposures ≈ 6200 Langmuirs (L) and at 10^{-5} Torr for higher exposures so that nothing can be said about the dependence, if any, of the adsorption on the pressure.

III. RESULTS

The EDC at 21.2 eV from clean Cd is given in Fig. 1; the spin-orbit-split $4d$ states are clearly seen, while the low featureless emission region extending up to the Fermi level is due to sp bands.⁶ The shape of the EDC makes it very easy to obtain

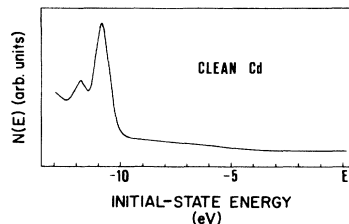


FIG. 1 Photoemission electron-energy-distribution curves, $h\nu = 21.2$ eV, from clean Cd. Initial-state energies are relative to the Fermi level ($E_F = 0$).

reliable difference EDC's when the sample is exposed to oxygen. The effect of oxygen exposure is clearly shown in Fig. 2 where difference EDC's up to 3200 L and two EDC's at higher exposures are collected. At the two highest exposures, difference EDC's are not necessary since the oxide is sufficiently thick that the photoemission from the substrate has marginal effect. The dashed regions of the spectra are those more affected by the uncertainty in the subtraction of the substrate contribution or of the secondary electron background. In any event, it is important to stress that these minor uncertainties have no influence on the discussions carried out in the present paper.

The electron-energy-loss spectra $N(E)$ of clean Cd, Cd exposed to 660-L oxygen, and Cd oxidized to saturation (7000 L) are given in Fig. 3. The analysis of the interaction between oxygen and cadmium based on energy-loss spectroscopy benefits greatly from the structure enhancement due to derivative techniques since some important structures in the $N(E)$ loss spectra are very weak. The

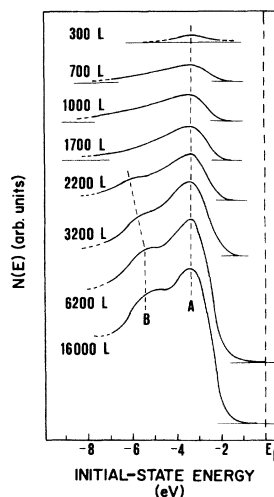


FIG. 2. The effect of Cd-O interaction at increasing oxygen exposures as seen from photoemission ($h\nu = 21.2$ eV). The curves for exposure ≤ 3200 L have had EDC of the Cd substrate subtracted out.

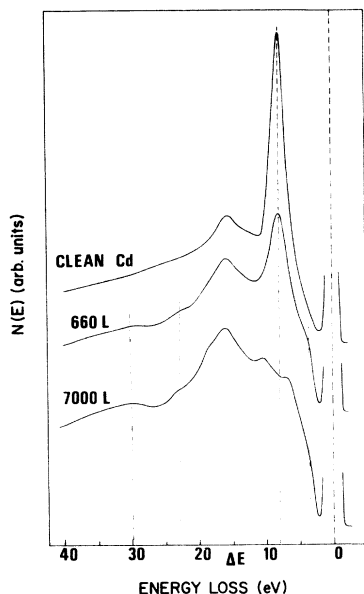


FIG. 3. The energy-loss spectra from the Cd-O system for increasing oxygen exposures.

first derivative of the energy-loss spectra at increasing oxygen exposure in the ΔE region (ΔE is the energy loss) up to 12 eV and from 12 to 44 eV are thus given in Figs. 4 and 5, respectively.

IV. DISCUSSION

A. Photoemission results

The UPS results of Fig. 2 show significant modifications in the shape of the EDC's with increasing exposure; viz., the oxygen-derived line becomes increasingly asymmetric and, around 2200 L, a shoulder *B* appears which shifts towards the main structure *A* at higher exposures. A saturation condition is reached at exposures greater than ≈ 6000 L. It is important to note that the saturation condition corresponds to the formation of the bulk oxide. The best proof of this is given by the electron-energy-loss spectrum taken at saturation and shown in Fig. 3. The spectrum at 7000 L is in excellent agreement with that of Hengehold and Pedrotti⁷ obtained using the same technique from a CdO single crystal fractured in the vacuum.

An important topic in metal-oxygen interactions is the surface arrangement of oxygen at low exposures (for the present case, up to ~ 1700 L). It is important to note that we did not observe any variation of the work function as judged from the beginning of the UPS spectra, while a decrease of the work function (≈ 0.3 eV) was seen at higher exposures. Although this method of obtaining the work function is not very accurate, this is an in-

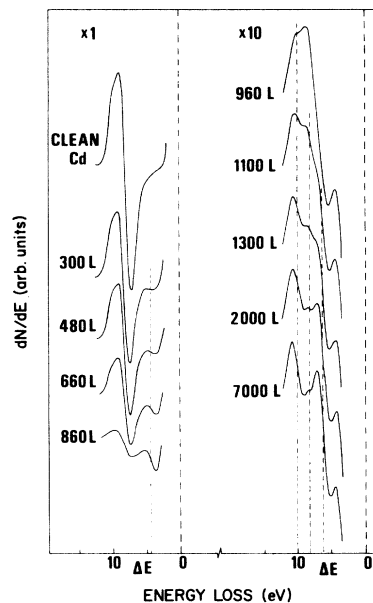


FIG. 4. The first derivative of the energy-loss spectra from the Cd-O system at increasing oxygen exposures in the energy-loss region up to $\Delta E = 12$ eV.

dication that oxygen is incorporated within the surface and is not located on top of the surface since, in this latter case, an increase of the work function is expected due to the surface dipole layer. The possibility that oxygen is incorporated into the Cd substrate is consistent with an anal-

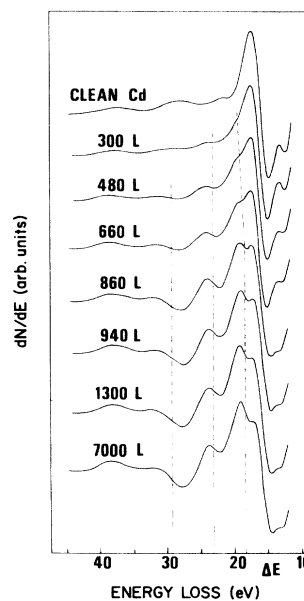


FIG. 5. The first derivative of the energy-loss spectra from the Cd-O system at increasing oxygen exposures in the energy-loss region from $\Delta E = 12$ to 44 eV.

ogous behavior established for Zn.⁴ As mentioned earlier, a peculiar feature in the low-exposure regime is the asymmetry of the oxygen-derived structure located ~ 3.5 eV below E_f . This feature could be due to several processes—among them the following:

- (1) For oxygen atoms incorporated within the surface, the P_z orbitals are not equivalent to the P_x and P_y .
- (2) Some oxygen-oxygen interactions via the substrate takes place with an effect on the line shape which grows stronger at increasing oxygen uptake.
- (3) Oxygen goes to nonequivalent sites due to the polycrystalline nature of the sample.

It is impossible to assess the relative weights of (1)–(3), but we can conjecture that the increase in the asymmetry indicates that (2) is very important. The use of a polycrystalline sample should be not very relevant in this connection since a similar asymmetry has been seen in the case of Zn for a single crystal.¹

An interesting feature in the UPS difference spectra (Fig. 2) is the appearance of the weak structure *B* at ~ 2200 L. Located initially at ~ -6.2 eV, with increasing exposure, *B* shifts to lower binding energy until a position typical of CdO is reached. This behavior can be understood by considering the properties of CdO. CdO is cubic and strongly ionic⁸ so that the valence states in the energy region of the structures *A* and *B* have a very high fraction of *p* character, thus giving a total bandwidth which is more narrow than in the presence of strong *sp* hybridization.⁹ When the oxide is sufficiently thick so that the local coordination of the atoms is almost that of rocksalt, the total bandwidth of the oxide phase is reduced and the position of structure *B* tends towards structure *A*. On the basis of this model, one can guess that several layers of oxide are necessary to create this situation and this implies that the coverage at the first appearance of structure *B* (~ 2200 L) is of the order of one monolayer. This estimate is consistent with a rough evaluation based on the attenuation of the Cd *4d* lines upon oxidation, although an accurate statement cannot be made, owing to the lack of data on the electron escape depths in CdO.

This argument is also supported by the results on the interaction of crystalline Zn with Te.¹⁰ With increasing Te exposure, the coordination becomes increasingly similar to that of zinc blende which is known to give the maximum bandwidth; in this case, an *increase* in the energy separation of structures analogous to *A* and *B* in the difference EDC's was observed.¹⁰ It is noteworthy that these results were obtained with single-crystal Zn. This is an indication that, in the present case, the use

of a polycrystalline Cd sample is not the origin of the binding energy shift of structure *B*.

Thus, the analysis of the valence state photoemission for the Cd-O system shows a very clear distinction between a low-exposure (isolated oxygen incorporated in the surface) regime and a high-exposure (oxide-formation) regime. This is interesting in connection with results already available for the oxidation of Zn. The physical situation at the surface is probably similar to Cd at low exposures when the oxide is not yet formed, and the shape of the density of states is strongly influenced by the interaction between isolated oxygen atoms and the metal. This fact is confirmed by the difference EDC's of Fig. 6 where the case of Zn plus 400-L oxygen² and Cd plus 700-L oxygen are compared and seen to be nearly identical. This comparison confirms the discussion given in Refs. 1 and 2 where a low-exposure region characterized by the interaction of Zn with almost isolated oxygen atoms has been identified before the ZnO formation. The fact that this distinction was not clear from the EELS data on Zn-O by Unertl and Blakely⁴ is probably due to the greater difficulty in clarifying the problem with this method. On the other hand, the low-energy electron diffraction (LEED) results of Unertl and Blakely indicate a formation of oxide from the beginning. This could be reconciled with the present argument by noting that, in a thin overlayer (e.g., two monolayers), the density of states is surely different from that of the bulk oxide since all the atoms of the oxide are surface or interface atoms. Probably the thickness necessary to obtain the oxide density of states is higher than that necessary to give approximately an oxide LEED pattern.

In connection with the spectra of Fig. 6, it is important to note that the peaks have been aligned to point out the similarity of the shapes; this implies an upward shift of the Zn scale of approximately 1.2 eV, since the oxygen *2p* structure appears in Cd at lower binding energies with respect to the Fermi level. Since CdO is known to

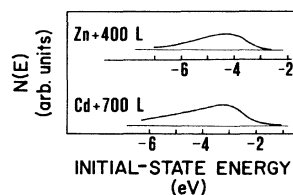


FIG. 6. A comparison of oxygen-induced photoemission structures ($h\nu = 21.2$ eV) in Zn and Cd exposed to 400- and 800-L oxygen, respectively.

be more ionic⁸ than ZnO, it could be that a greater charge transfer takes place in Cd-O than in Zn-O.

B. Energy-loss results

The general picture given above also results from analysis of the EELS results, although the recovery of information on valence states is more complicated than in UPS. Figure 3 shows EELS spectra for the clean Cd substrate, for the case of 660-L exposure to oxygen (i.e., in the chemisorption region), and at saturation (7000 L). At 660 L, one notes a marked decrease of the plasmon loss peak¹ of the substrate at ≈ 8 eV and three very weak structures at $\Delta E = 4.4, 23,$ and 30 eV. The structure at 4.4 eV is necessarily connected with transitions from states derived from oxygen $2p$ electrons to the lowest conduction band. From energy considerations, this loss structure corresponds to transitions from those states responsible for peak *A* in the valence EDC's of Fig. 2. In this connection, it is useful to consider the derivative of the loss spectra. As is well known, the loss peaks appear in the derivative spectra as inflection points which are often more easily seen—as pointed out in Fig. 4 where the region up to $\Delta E = 12$ eV is given. This region is the most interesting for the study of the transition from the chemisorption to the oxide regime. The increase of the structure at 4.4 eV with exposure is clearly seen, although no conclusion can be drawn about the line shape. The formation of the oxide can also be followed from the gradual appearance of the structures at 6.2, 8.3, and 10.2 eV which are typical of the oxide and which correspond within the experimental accuracy to those observed by Hengehold and Pedrotti⁷ and to the optical structures seen by Freeouf.¹² The spectrum saturates around 7000 L, but already at 1300 L is very similar to that at saturation. It is thus possible to state that, in agreement with the UPS results, the EELS results also show a progressive transition towards the bulk oxide. However, no clear counterpart to the evolution of the UPS structure *B* of Fig. 2 is seen in the EELS case.

The loss structure around 16 eV is not very useful in the analysis of the metal-oxygen interaction since the separation between the substrate and the oxide contribution is difficult, owing to the interference of Cd loss structure at ≈ 16 eV (see Fig. 3) with the surface plasmon peak of CdO at ≈ 15.9 eV.⁷

At higher ΔE (see Fig. 5), the most interesting

structures are those at $\approx 18, 23,$ and 29 eV. The latter two structures appear at constant ΔE , while the former one shows a small shift at increasing coverages; this shift will not be discussed since it could be due to an overlap of loss structures. It is interesting to note that these structures appear from the very beginning of the exposure so that they must contain some contribution from transitions involving states of isolated or nearly isolated adatoms, i.e., before the formation of the oxide (oxygen $2p$ and $2s$ initial states). This fact is particularly relevant for the structure at $\Delta E = 23$ eV which in CdO is known to be due to a plasmon as seen with EELS⁷ and with optical spectroscopy.¹² Thus, the present results show that loss structure is observed at ≈ 23 eV for the Cd + O₂ system, but the character of this structure (transitions involving isolated oxygen adatoms and/or plasmon loss) depends on how far the surface oxidation has progressed. It is important to note that this condition conclusion would hardly be possible in the absence of energy-loss spectra in the chemisorption regime.

At higher ΔE , a loss structure at 38.5 eV is found whose analysis is complicated by the presence of a substrate contribution at nearly the same energy. The discussion of this structure would require a theoretical investigation on high-energy transitions, which is not available at present.

V. CONCLUSION

In conclusion, we have reported the first results on the oxidation of metallic Cd performed using the surface-spectroscopic techniques of UPS and EELS. These methods indicate a clear passage from a chemisorption regime to an oxide regime. In UPS, the $2p$ resonance due to isolated chemisorbed oxygen atoms is clearly seen. At increasing coverages, the line shape becomes asymmetric and a satellite structure appears at higher binding energy. The fingerprint of the oxide at the surface is the reduction of the binding energy of this satellite structure. This is attributed to a narrowing of the total valence bandwidth of the system, owing to the cubic coordination of the oxide. In addition to supporting the general trends in the Cd-O interaction observed using UPS, the EELS results give new insight into loss structure previously observed at 23 eV in CdO. The precise character of this loss structure—transitions involving isolated oxygen adatoms and/or plasmon loss—depends on how far the surface oxidation has progressed.

*Present address: Varian Associates, Solid State Laboratories, Palo Alto, California 94303.

¹I. Abbati, L. Braicovich, R. A. Powell, and W. E. Spicer, in *Proceedings of the 7th International Vacuum Congress and the 3rd International Conference on Solid Surfaces, Vienna, 1977*, edited by R. Dobrozemsky, F. Rüdener, F. P. Viehböck, and A. Breth (Austria, 1980), pp. 919–922.

²I. Abbati, L. Braicovich, and R. A. Powell, *Surf. Sci.* 87, L243 (1979).

³W. N. Unertl and J. M. Blakely, *J. Colloid Interface Sci.* 55, 320 (1976).

⁴W. N. Unertl and J. M. Blakely, *Surf. Sci.* 69, 23 (1977).

⁵J. Lagowski, M. Lichtensteiger, and P. M. Williams, *Surf. Sci.* 84, L223 (1979).

⁶R. W. Stark and L. M. Falicov, *Phys. Rev. Lett.* 19, 795 (1967).

⁷R. L. Hengehold and F. L. Pedrotti, *J. Appl. Phys.* 47, 287 (1976).

⁸J. C. Phillips, *Rev. Mod. Phys.* 42, 317 (1970).

⁹S. T. Pantelides, *Phys. Rev. B* 11, 5082 (1975).

¹⁰I. Abbati, L. Braicovich, G. Ciucci, and P. Perfetti, *J. Vac. Sci. Technol.* 16, 863 (1979).

¹¹B. Feuerbacher and I. Fitton, *Phys. Rev. Lett.* 24, 499 (1970).

¹²J. L. Freeouf, *Phys. Rev. B* 7, 3810 (1973).