

# Carbon Contaminant Buildup and Sputtering Behaviour on Zinc Oxide During XPS Examination

M. Mintas\* and G. W. Filby

Kernforschungszentrum Karlsruhe, Institut für Radiochemie

Z. Naturforsch. **36a**, 140–143 (1981); received December 11, 1980

The effect of argon and oxygen sputtering on carbon contaminant buildup on ZnO during XPS (X-ray photoelectron spectroscopy) analysis has been examined. Argon and oxygen sputtering cause a rapid decline in hydroxyl oxygen and contaminant carbon content at the surface. Reduction to metallic zinc is not observed. In a carefully baked instrument after sputtering a stable clean surface could be maintained over several hours of analysis.

## Introduction

During the course of our XPS studies of heterogeneous decomposition of Freons on ZnO surfaces we found it necessary to investigate the oxide with regard to i) its behaviour under ion sputtering and ii) the magnitude and variation of the carbon contaminant. Both points are related in that we employed Ar<sup>+</sup> ion sputtering for cleaning the surface prior to actual experiments.

Sputtering, however, not infrequently leads to physical and chemical alteration of the surface and underlying layers (mixing, roughening, cratering, change in oxidation state) and contaminant peaks have been reported to falsify sample peaks rendering even semiquantitative evaluations difficult. The contaminant may be present prior to introduction of the sample into the spectrometer or can arise within its source during investigation. In this report we show that, on simultaneous comparison of conducting and non-conducting surfaces (ZnO and Au) carbon contaminant can be made very small and buildup so slow as not to effect quantitation within our usual measurement and acquisition times. Additionally the gold surface is, once cleaned, so stable that it can be employed as an internal standard.

## Experimental

### I. Material and Sample Preparation

Zinc oxide was obtained from the New Jersey Zinc Company (quality SP500) and was Soxhlet

extracted for one week prior to usage. Spectra were determined on samples formed as  $2 \times 6 \times 12$  mm rectangular tablets prepared at 200 kp/cm<sup>2</sup> and subsequently glued onto gold foil (0.5 mm) with Torrseal adhesive (Varian). Approximately equal areas of ZnO and Au were exposed to the analysing X-rays. The whole was then mounted onto the retractable sample holder and placed in the preparation chamber of the spectrometer for treatment.

Thus the gold foil was maintained in good electrical contact with the spectrometer and the ZnO surface, by virtue of its thickness and low conductivity, isolated from it.

In this way contaminant build up on the exposed conductor (Au) and insulator surface could be simultaneously followed by means of alterations in the respective ESCA peaks.

### II. Instrumental

Spectra were obtained on an AEI ES 200 (hemispherical retarding analyser) spectrometer equipped with an Mg K  $\alpha$  X-ray source.

The source gun had been completely reinstalled, reconditioned and the instrument subjected to a full bake-out prior to these experiments. The source was maintained water cooled (10 °C) for all measurements. The spectrometer had a base pressure of  $5 \times 10^{-8}$  Torr in the analyser chamber. For sputter etching, the gas pressure was maintained at  $5 \times 10^{-5}$  Torr (Varian leak valve) and the ion gun (Physical Electronics Inc.) set at 6 kV and 40  $\mu$ A at normal incidence. The oxide surface can be etched at several Å/min under these conditions. The ESCA intensities are expressed as integrated peak areas uncorrected for ionisation sensitivity.

\* Visiting scientist from the University of Zagreb, Faculty of Technology, Department of Organic Chemistry.

Reprint requests to Dr. W. G. Filby, Institut für Radiochemie, Kernforschungszentrum Karlsruhe, Postfach 3640, D-7500 Karlsruhe 1.



## Results and Discussion

### I. Argon and Oxygen Sputtering

The XPS spectra in the O (1s) and C (1s) regions of ZnO before and after sputtering are shown in Figure 1. It is by now well established that an

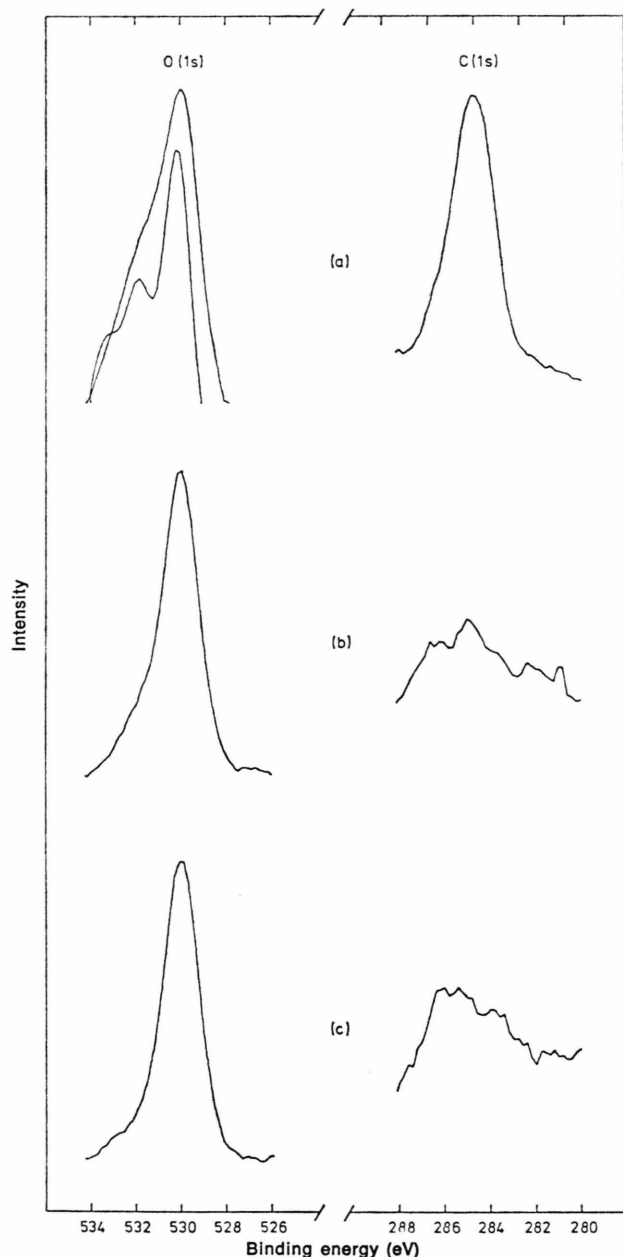


Fig. 1. XPS spectra of O (1s) and C (1s) levels on ZnO surfaces a) prior to sputtering, b) after sputtering with  $\text{Ar}^+$  ions (6 kV, 40  $\mu\text{A}$ , 20 mins), c) after sputtering with  $\text{O}_2^+$  ions (6 kV, 30  $\mu\text{A}$ , 20 mins).

O (1s) BE of ca. 530 eV indicates lattice oxide structure while that for a hydroxide lies 1.5–2.0 eV higher [6, 11]. Thus we conclude that our specimens initially contain surface hydroxide [12] (down to ca. 10 Å — the escape depth at ca. 700 eV) [16] amounting to ca. 10% of bulk oxygen. The chemical changes induced by even very drastic  $\text{Ar}^+$  bombardment are seen to be minimal, being restricted to an almost complete removal of the hydroxide oxygen within 20 min of treatment. Simultaneously an important clean up effect is observed — the Zn (2p), O (1s) oxide and Au (4f<sub>7/2</sub>) peaks (Fig. 2) are almost doubled in intensity, while that of C (1s) loses its contours and the counts fall to little above the background level. This may be interpreted as due to simple physical sputtering removing the top surface hydroxide and carbon contamination from the ZnO and ZnO/Au surfaces respectively and revealing the underlying oxide component.

“Cleaning up” is complete after this procedure and no further changes can be observed even by intensive  $\text{O}_2^+$  ion sputtering (20 mins, 6 kV). In accordance with the prediction of Kim *et al.* [7] further chemical reduction was not evidenced by any alterations in the Zn (2p) or O (1s) peaks [10].

### II. Behaviour of Carbon Contaminant on Untreated and Sputtered Surfaces

A typical feature observed on all untreated ZnO/Au samples investigated was the constancy of the Au (4f<sub>7/2</sub>) [13] and the increase of the C (1s) peaks as a function of measuring time up to 4 hrs X-ray exposure. During a ca. 4 hr residence in the analysing chamber the C (1s) (i.e. total carbon contaminant on ZnO and Au surfaces) increases while the Zn (2p) and O (1s) decrease and the Au (4f<sub>7/2</sub>) remains constant within the error of our experiments. The latter implies preferential contaminant build up on the oxide surface.

The behaviour of the reference peaks from samples after sputtering is strikingly different, whereas in untreated samples contaminant levels reached a maximum and reference peaks (Zn, O, Au) a minimum after ca. 4–5 hrs sputtered samples revealed no evidence of any such trend (Fig. 2) in this time period).

### III. Rationale

In the following we attempt to rationalise these findings according to currently accepted knowledge

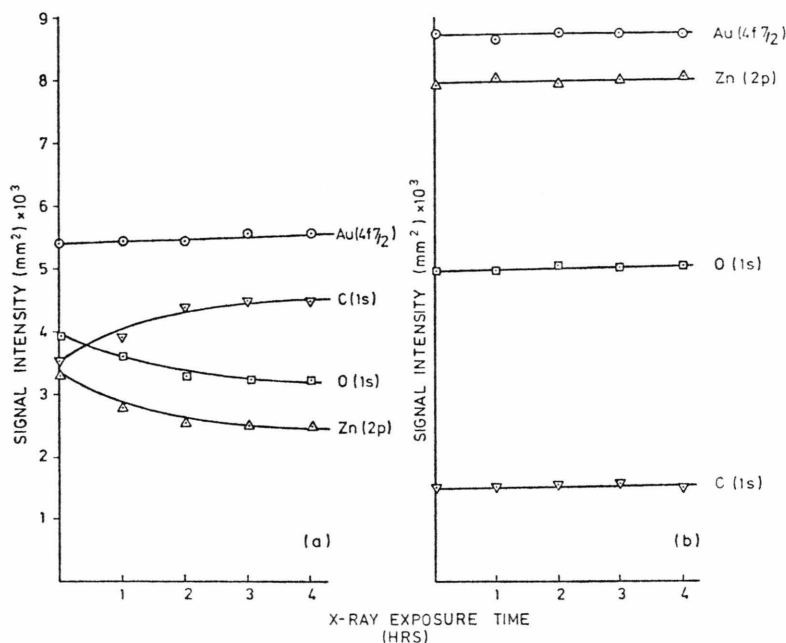


Fig. 2. Effect to X-ray exposure on peak intensities in i) untreated ZnO, ii) ZnO tablet after sputtering with  $\text{Ar}^+$  ions (6 kV, 40  $\mu\text{A}$ , 20 mins).

on the behaviour of specimens under XPS examination. The major source of hydrocarbon contaminant in our type of spectrometer is, according to Clark *et al.* [9], "boil off" from the X-ray tube window. Even when extremely well baked out our apparatus should be no exception.

Under our conditions (newly installed and conditioned source) this hydrocarbon contaminant probably arises initially via adsorption of residual gases from the diffusion pump oil onto the cooled source window. Thus the differences in the behaviour towards contaminant build up on unsputtered and sputtered ZnO surfaces must arise from altered sticking coefficients towards carbon containing

species present in the analyser. We favour an X-ray induced free radical reaction to form the carbonaceous, possibly polymeric deposit. Such a reaction would be initiated by radiation chemical scission of the surface hydroxide resulting in the formation of active hydroxyl radicals. These species, when available, can react with the carbonaceous impurities forming the detectable products. After removal of the hydroxide film by sputtering contaminant build up on ZnO is either completely unfavoured by extremely low sticking coefficients (unlikely) or takes place via processes with much longer half lives than could be observed within the time scale of our experiments [14].

- [1] W. G. Filby, M. Mintas, and H. Güsten, German-yugoslav Symposium on environmental chemistry in air and water, Rovinj, Yugoslavia, May 12–14, 1980.
- [2] J. W. Coburn, *J. Vac. Sci. Technol.* **13**, 1037 (1976).
- [3] K. S. Kim, W. E. Baitinger, J. W. Amy, and N. Winograd, *J. Elec. Spectr.* **5**, 351 (1976).
- [4] R. Holm and S. Storp, *Appl. Phys.* **12**, 101 (1977).
- [5] E. S. Brandt, D. T. Untereker, C. N. Reilly, and R. W. Murray, *J. Elec. Spec.* **14**, 113 (1978).
- [6] T. J. Chuang, C. R. Brundle, and D. W. Rice, *Surf. Sci.* **59**, 413 (1976); *ibid.* **60**, 286 (1976).
- [7] K. S. Kim and N. Winograd, *Surf. Sci.* **43**, 625 (1974). These authors found that the behaviour of metal oxides under  $\text{Ar}^+$  bombardment could be well predicted by the room temperature free energy of formation  $\Delta G_f^0$ . All oxides with  $-\Delta_f^0$  below 60 kcal/mole were reduced by exposure to  $\text{Ar}^+$  while those with  $-\Delta G_f^0$  above 108 kcal/mole are stable. The  $\Delta G_f^0$  for ZnO is  $-76$  kcal/mole. The reliability and theoretical basis of these findings has recently been questioned [8].
- [8] T. J. Chuang, C. R. Brundle, and K. Wandelt, *Thin Solid Films* **53**, 19 (1978).
- [9] D. T. Clark, H. R. Thomas, A. Dilks, and D. Shuttlerworth, *J. Elec. Spectr.* **10**, 455 (1977).
- [10] The chemical shift between  $\text{Zn}^0$  in metallic zinc and  $\text{Zn}^{2+}$  in zinc oxide amounts only to only few tenths of an eV. Thus reduction would, in any case, be difficult to detect. The only difference in the Zn (2p) signals from Zn and ZnO is the slightly broader halfwidth (0.3 eV) in the former [11].
- [11] E. Schön, *J. Elec. Spectr.* **2**, 75 (1973).

- [12] The completely hydroxylated surface of ZnO evacuated at 25° has 5.5 water molecules or 11.10 hydroxyl groups per nm<sup>2</sup>. This is reduced to 1.06 hydroxyl groups per nm<sup>2</sup> after evacuation at 600 °C. M. Nagao and T. Morimoto, J. Phys. Chem. **84**, 2054 (1980).
- [13] Brandt et al. [5] also observed a reduction in the intensity-time change on sputter-cleaned gold.
- [14] The time for 50% attenuation of signal at 10<sup>-7</sup> torr pressure and sticking coefficients of  $5 \times 10^{-1} - 10^{-3}$  can range from 6 min—6 hr [15].
- [15] J. A. Becker, in F. Seitz and D. Turnbull (Eds.), Sol. State Physics, Vol. 7, Academic Press, New York N. Y. 1958, p. 379.
- [16] C. R. Brundle, Surf. SCI., **48**, 99 (1975).