

CCA-1297

YU ISSN 0011-1643

UDC 541.183

Note

Surface Charging of Zinc Oxide During XPS Examination

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Received December 16, 1980

Surface charging of zinc oxide during XPS examination has been studied. The magnitude of the charge is 0.4—0.6 eV at room temperature and decreases at higher temperature to almost zero (nominal 0.1 eV at 300 °C). Reproducible BE values can only be achieved after correction for this charging. Possible mechanisms are briefly discussed.

INTRODUCTION

During the course of an XPS study of the heterogeneous catalysed decomposition of Freons¹ it became necessary to investigate possible surface charging of the zinc oxide specimens involved. As far as the authors are aware the literature contains no reference to this specific point. Charging of samples is extremely frequent and metal oxides, especially semiconductors often charge up to significant extents during XPS examination. It was thus of importance to determine whether the accompanying BE shifts could cast doubt on our experimental conclusions. The mechanism of steady state charge formation has been outlined as follows²⁻⁵. Primary and secondary electron emission result in a positive surface charge unless counterbalanced by a neutralising electron current to the sample. Currently the level of charging achieved is believed to be related to i) the X-ray flux and its energy, ii) surface conductivity and iii) the induced flux of slow electrons in the vacuum space around the sample.

In this note we report briefly on the charging behaviour of zinc oxide tables under the experimental conditions employed in our Freon work.

EXPERIMENTAL

The experiments were carried out with zinc oxide (New Jersey Zinc Company, high purity grade SP 500) which was Soxhlet extracted with bidistilled water for 1 week prior to use. The powdered substance was pressed (200 kp/cm²) into rectangular tablets (12 × 6 × 2 mm) using a specially constructed die and hydraulic press⁹. For XPS measurement the tablet was carefully glued (Torrseal low vapour pressure adhesive) onto gold foil (0.5 mm) and the whole mounted onto the retractable sample shaft of the spectrometer by means of two holding screws. The orientation of the sample during measurement was adjusted (45° to analyser entrance) such that sample, peripheral gold foil and screwheads were all visible thereto. The gold thus functioned as an internal standard. Repeated binding energy determinations thereof were reproducible to ± 0.1 eV. The spectrometer employed was an AEI ES-200 using a Mg K (α)

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source (1253.6 eV). The X-ray voltage was set at 15 kV and 225 W in all experiments, somewhat above that previously observed for maximum charging⁴ (4 kV, 160 W). Lines were scanned (20 eV) until counts above background amounted to $10-15 \times 10^3$.

The spectrometer work function was chosen so as to place the Au ($4f_{7/2}$) line at 83.7 eV. The observed line positions were corrected for charging by using the position of the C (1s) line from adsorbed hydrocarbon. The assumption is then that the carbon is present as an overlayer thin enough to sense the potential of the sample surface. The value assumed for electrical neutrality is 284.6 eV this being the C (1s) value of an overlayer present on an inert conductor (e.g. Au). Although it is well known that the charging effect is very instrument dependant, the validity of this method for a single instrument has been amply demonstrated⁵.

RESULTS AND DISCUSSION

Table I shows two sets of typical data* for ZnO tablets under XPS examination. Clearly during measurements at room temperature under our instrumental conditions (see Experimental) a steady state charge of somewhat over 0.5 eV can be expected on the ZnO surface. Increasing the measurement temperature brings about a gradual decrease in charge until at ca. 300 °C (our maximum measuring temperature) the charge probably reduces to zero. This effect was observed several times with different samples, the value of the charge for a given specimen and temperature always being nearly identical although the initial room temperature value sometimes varied by 0.1–0.2 eV (cf. Expt Ib). Evacuation and increasing the temperature prior to measurement at room temperature resulted in a residual static charge marginally higher than the initial one (cf. Expts Ia, Id; IIa, IId). Of especial interest and importance to us for our room temperature measurements however was the simplicity of charge correction. Subtraction of the C (1s) static charge from the »charge

TABLE I

Real and Apparent Binding Energies* for Zinc Oxide During XPS Examination
MgK (α) Source (1253.6 eV), Uncharged C (1s) = 284.6 eV

Expt.-No.	Measurement Temperature °C	Apparent Binding Energy			Charge (eV)	Corrected Binding Energy ^a	
		Zn (2p)	O (1s)	C (1s)		Zn (2p)	O (1s)
I (a)	25	1022.77	531.16	285.23	0.63	1022.14	530.53
	(b)	140	1022.37	530.67	284.9	1022.07	530.37
	(c)	240	1022.31	530.7	284.84	1022.07	530.46
	(d)	25	1022.80	531.26	285.31	1022.09	530.55
II (a)	25	1022.48	530.84	284.97	0.37	1022.11	530.47
	(b)	140	1022.33	530.69	284.9	1022.03	530.39
	(c)	300	1022.19	530.43	284.7	1022.09	530.33
	(d)	25	1022.65	531.04	285.12	1022.13	530.52

* Binding energies (eV) are the average of three determinations

^a Schön¹⁰ and Vesely and Langer¹² give Zn($2p_{3/2}$) = 1021.7 ± 0.2 ; 1021.38 ± 0.21 and O (1s) = 530.6 ± 0.2 and 530.6 respectively. Schön observed surface charging of at most 0.3 V for ZnO at 25 °C.

* These are the extreme values observed during examination of ca. 25 different samples.

shifted« Zn (2p) and O (1s) values yielded reproducible BE values even after 2–3 heating and cooling cycles⁶.

A somewhat pictorial consideration of the mechanism of charge formation aids understanding of the effects described. The currently widely accepted mechanism suggests that the positive charge arising from primary and secondary photoemission increases until balanced by currents from the vacuum space and/or sample support. In our work involving thick semiconductor tablets the latter should not be important. However the total photoemission will, on account of the varying tablet preparation be very different from states on thermal activation resulting in an increased hole concentration in secondary emission will vary greatly and account for the differing initial charging levels of the various specimens. Similarly although the instrumental flux will be nearly identical from measurement to measurement the sticking coefficient of the surface may vary broadly. Wagner⁵ has indicated the importance of hydrocarbon electron affinity in determining the charge magnitude.

The effect of temperature is to remove the charge by increasing the surface conductivity^{4,8}. The mechanism of this thermal activation is however unclear and two explanations are currently under discussion i) charge removal is due to increased hole mobility⁷ and ii) an increased occupation of shallow trapping states on thermal activation resulting in an increased hole concentration in the valence band⁸. It is not possible on the basis of our experiments to decide definitively for one or the other mechanism. Suffice it to say that the first explanation will require the neutralising current to balance the emission current at higher temperatures. This latter is probably operative in our experiments (IId).

Acknowledgement. — This work was performed on the basis of a German-Yugoslav scientific cooperation. The financial support by the Internationales Büro, Kernforschungsanlage, Jülich is gratefully acknowledged.

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SAŽETAK**Površinsko nabijanje cinkovog oksida tokom XPS istraživanja***M. Mintas i W. G. Filby*

Proučavano je površinsko nabijanje cinkovog oksida tokom XPS istraživanja. Veličina naboja je 0.4—0.6 eV kod sobne temperature i pada kod nižih temperatura na gotovo nulu (neznatnih 0.1 eV kod 300 °C). Reproducibilne BE-vrijednosti mogu se dobiti samo korekcijom za to nabijanje. Ukratko su diskutirani mogući mehanizmi.

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Prispjelo 16. prosinca 1980.