SURFACE CONCENRATION AND SURFACE SEGREGATION EFFECTS IN CATALYSTS BY XPS

A) SURFACE CONCENTRATION ANALYSIS BY X-RAY PHOTOELECTRON SPECTROSCOPY:

The measurement of surface atomic concentrations is an important potential application of X-ray photo-electron spectroscopy (XPS). The XPS peak intensities are proportional, in the first approximation, to the surface atomic concentrations and the photo-ionization cross sections. There have been experimental measurements of photo-ionization cross sections using XPS peak intensities from reference materials . These studies have shown that the potential for surface quantitative measurement exists but is limited by difficulties in accurate peak intensity measurement.

A calculation of the surface composition from X-ray photo electron intensities requires a set of equations for the intensities that reflects the true surface layering. In the following, the expressions for the XPS intensities from a general system of several homogeneous layers are developed. The equations for the XPS intensities are derived assuming an exponential attenuation of electron intensity during passage through the solid. The photoelectron intensity from an incremental layer at depth z into the surface is given by

$dI_i = Io \exp(-z / g \gamma i)\, dz$

where is the number of photoelectrons generated per unit volume, i is the mean free path of electrons of kinetic energy Ei, and g is a specimen-spectrometer geometrical factor that takes into account the angle of escape of the electron with respect to the surface normal. The number of electrons generated per unit volume, Io is given by

$$Io = Ki\, \sigma i\, Xi$$

where K*i* is a constant instrumental factor including X-ray flux, Xi is the atomic

volume concentration of element i and is the σi photoionization cross section for the photoelectron observed for element i.

Example of XPS analysis on ZnO catalyst in methanol reaction

The first step in applying the equations to the methanol & ZnO system is to calculate the surface composition of the starting material (an electron beam cleaned ZnO). This ZnO contained carbon at the surface. A surface oxygen component was also indicated by an oxygen (1s) photo electron peak at about 1.7 eV higher binding energy than the principal oxygen (1s) peak.The calculation performed by known parameters.

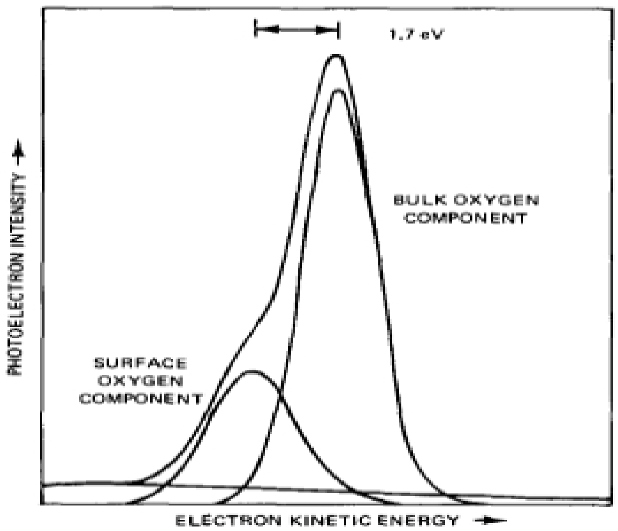

Fig. 3. The O(1s) photoelectron peak for ZnO that has been cleaned by electron beam heating.

B) SURAFCE SEGREGATION ANALYSIS BY X-RAY PHOTOELECTRON SPECTROSCOPY:

Using example of XPS Investigation of Segregation of Sb in SnO2 Powders

Tin-oxide powders have been widely used for technical applications such as gas sensors, catalyst, or as transparent conductive oxide in the field of optoelectronic devices. Dopants such as antimony, indium, or fluorine are added to improve the electrical or sensing properties.

Tin and antimony can co-precipitate from solution in a controlled precipitation process. Antimony is added in tin-oxide powders to reduce the resistivity. Antimony phase has not been found until the amount of doping 20 mol% antimony. But even less than 20 mol% Sb is added, not all the antimony atoms can be built in lattice on the tin sites. Strong segregation of dopping atoms at the grain surface has been reported. It is revealed that enrichment of dopant depends on the additive's concentration and the preparation technique. The kinetics of segregation process in SnO2 has been studied.

X-ray photoelectron spectroscopy (XPS) were applied to study the doping components. The conductive powders or films were usually annealed at 500 ^oC in industry production, while antimony doped powders were annealed at temperature higher than 700 ^oC in literature. The segregation behavior of annealing at 500 ^oC is uncertain. A model has been proposed in previous researches, and the bulk concentrations have been calculated based on the model for Sb doped SnO2 powders annealed at different temperature. But uncertainties still exist on the bulk concentration. Therefore further studies on antimony doped tin-oxide(ATO) are still necessary. This paper presents the enrichment of do-pant depending on the concentration as annealing at 500 ^oC. Moreover, the content and valence of doping element Sb have been investigated in accordance with temperature. Variation of the conductivity of SnO2 powders is also discussed.

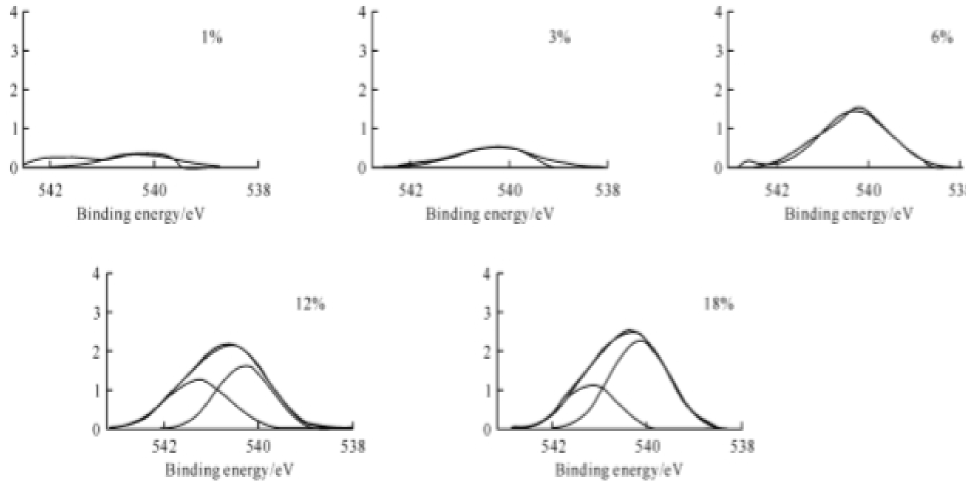

Fig.2 Peak fit of $Sb3d_{3/2}$ as a function of total doping concentration

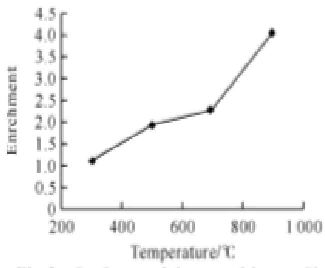

Fig.3 Surface enrichment of dopant Sb on SnO_2 grain depending on annealing temperature(SnO_2 doped with 6 mol% of antimony)

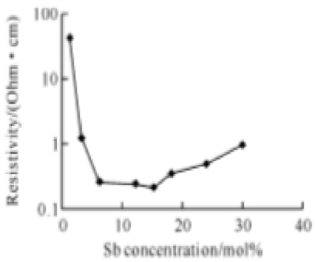

Fig.4 Resistivity of doped oxides in dependence on doping concentration

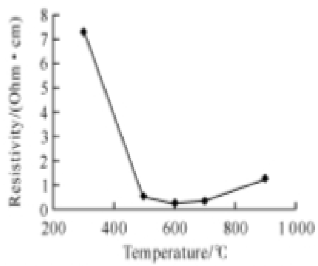

Fig.5 Resistivity of doped tin oxides as a function of the annealing temperature(powders containing 6 mol% of Sb)

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