Changes of Auger Parameter in doped SnO$_2$ powders

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1. Introduction

The Auger parameter is often used for binding state characterisation using XPS because it does not depend on surface charging. This parameter was introduced by Wagner [1] and is defined as:

$$\alpha' = E_K(jkl) + E_B(i) \qquad (1)$$

$E_K(jkl)$ is the kinetic energy of the Auger transition jkl and $E_B(i)$ is the binding energy of the photoelectron emitted from atomic level i. The change of Auger Parameter of an element in various substances is connected with the change of relaxation energy R^{ea}. The relation between both values can be written as:

$$\Delta\alpha' = 2\Delta R^{ea} \qquad (2)$$

The changes of relaxation energy and connected with it changes of Auger parameter can be caused by a lot of various factors, for example change of oxidation state [2], doping and connected with it changes of sample properties [3] as well as building of surface layers [4]. In the present study we show the influence of this factors on the Auger parameter for doped SnO$_2$ powders with respect to optimise their electrical properties [5, 6].

2. Experimental

1. Samples:
➢ In, Sb and Nb doped SnO$_2$ powders synthesised from precipitated β-stannic acid and fired at 900^{0}C under oxygen atmosphere.[6]
➢ SnO$_2$ mono-crystal
2. Measurements conditions:
➢ XPS System PHI 5600 CI, Al - K$_\alpha$, 350 W non-monochromatized X-ray radiation
➢ pass energy 11 eV, energy step width 0.1 eV, system pressure < 10^{-7} Pa

3. Results and Discussion

1. Oxidation state
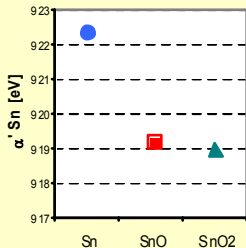

Fig.1 Sn Auger Parameter for various tin compounds

The change of the chemical state of an element can very strongly influence its Auger parameter. The Sn α' calculated for SnO$_2$ in the present study amounts to 918.9 eV. The Sn Auger parameter for SnO lies at about 919.2 eV [4] and that for metallic tin at 922.3 eV. So the formation of other chemical states than SnO$_2$ by doping will be expressed in a shift of Sn α'. However the XRD measurements have shown, that at low doping concentration only tin dioxide phase is found. At higher dopant concentrations additional dopant oxide particles are created, but no metallic tin or tin monoxide is detected.
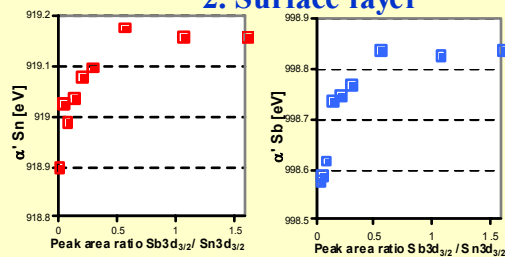
2. Surface layer

Fig. 2 The change of the Auger Parameter during formation of an Sb$_2$O$_x$ layer on an SnO$_2$ mono-crystal

The formation of oxide layers on the surface can influence the Auger parameter due to forming of M-O-M chemical bonds at the interface.
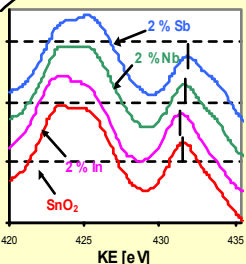The observed changes by evaporating of antimony oxide on SnO$_2$ mono-crystal amount to about 0.3 eV.

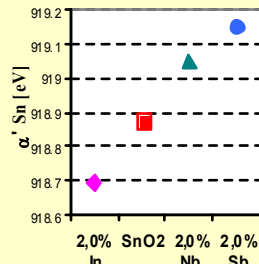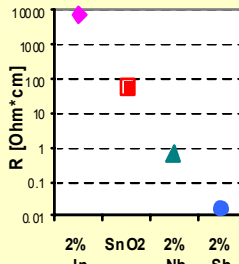Fig. 3 The change of Sn MNN line shape by doping

Fig.4.Correlation between Sn Auger Parameter (a) and electrical properties (b) of with 2 mol% doped tin oxide powders
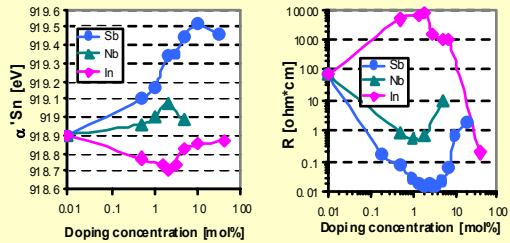
3. Dependence on electrical properties

Fig.5.Comparison of Sn Auger Parameter (a) and electrical properties (b) of doped tin oxide powders in dependence on doping concentration

Fig.6. The changes of Sb (a) and In (b) Auger Parameter in doped tin oxide powders in dependence on doping concentration

The influence of doping on position and shape of Sn MNN Auger line can be observed already at low doping concentrations Fig. 3 shows a comparison of Auger lines for various doped SnO$_2$ powders at doping concentration of 2 mol%. A shift of the Auger line to higher BE by doping with In and to lower BE by doping with Sb and Nb is detected. As reference line for the BE scale the Sn3d$_{5/2}$ peak is used. In accordance the Auger parameter is at lower values for In doped samples and higher values for Sb and Nb doped samples with respect to pure SnO$_2$ (Fig 4a).

A connection of α' changes with change of electrical properties caused by doping is observed (Fig 4b). A good qualitative proportionality for α' and the resistivity of the powders is observed for the whole studied concentration range (Fig 5). The connection of electrical properties with relaxation energy can be described by eq.3 [7].

$$R^{ea} = (1 - \varepsilon^{-1}) \times e^2 / 2r_0 \qquad (3)$$

where ε is the static dielectric constant, e one unit of charge and r$_0$ the effective electron screening distance.

SnO$_2$ is a n-semiconductor, where free electrons are reliable for conductivity. Doping with pentavalent Sb and Nb leads to increasing of conductivity by increasing of free electron density. In this case r$_0$ decreases, which leads to the observed increasing of relaxation energy. On the other hand doping with trivalent In decreases the number of free electrons followed by a decreasing conductivity. Therefore a decrease of the relaxation energy is observed.

According to that the Auger parameter of the doping elements In and Sb (Fig. 6) for the studied powders show a quite similar course as the α' for Sn discussed before (see Fig. 5a).
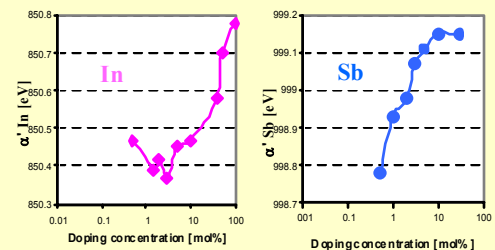
4. Conclusions

⇒ The changes of Auger parameter can give general information about differences in the electrical properties between variously doped SnO$_2$ powders.
⇒ SnO$_2$ doping with pentavalent elements lead to increasing of conductivity and parallel to an increasing of the relaxation energy. On the other hand doping with trivalent elements cause decreasing of conductivity and in accordance with it R^{ea} occurs at lower values.
⇒ Due to the similar behaviour of Auger parameter of Sn and of the dopants it can be expected that in the studied samples there are not significant changes of chemical states.

5. References

1. C.D. Wagner, Farad. Discuss. Chem. Soc., 60, 291 (1975)
2. D.Briggs, M.P. Seah, Practical Surface Analysis, Volume 1 - Auger and X-ray Photoelectron Spectroscopy, 1990
3. A. Von Richthofen, R. Cremer, R. Domnick, D. Neuschütz, Thin solid Films 315, 66 (1998)
4. V.M. Jimenez, J.A. Mejias, J.P. Espinos, A.R. Gonzalez-El ipe, Surface Science 366, 545 (1996)
5. D. Szczuko, J. Werner, G. Behr, S Oswald, K. Wetzig, Surface and Interface Analysis, 31, 484 (2001)
6. W. Fliegel, G. Behr, J. Werner, G. Krabbes, Sensors and actuators B, 18, 474 (1994)
7. W.F. Egelhoff, Surface Science Reports 6, 253 (1987)