Supplementary Information

Dopant Mediated Surface Charge Imbalance in Enhancing Performance of Metal Oxide Chemiresistive Gas Sensors

Nirman Chakraborty and Swastik Mondal[*]

CSIR-Central Glass and Ceramic Research Institute, 196, Raja S. C. Mullick Road, Jadavpur, Kolkata-700032, India

Corresponding author: swastik_mondal@cgcri.res.in

Calculations regarding estimation of excess surface charge per formula unit

Case 1: Vanadium doped SnO_2 nano systems

Step 1: *Estimation of area under the curve from deconvoluted XPS signals.*

In this method, the first step is to deconvolute an XPS signal into maximum possible curves as expected from experiments. Then, the area under the curves are to be noted when optimum fitting has been achieved.

For example, we shall discuss the case of Sl. No. 2 in Table 1 of manuscript. This is a case of vanadium doped tin oxide ammonia sensors. After deconvoluting the Sn 3d and V 2p curves, following information for both compositions were available:

Table 1: Quantitative values of area under curve obtained from XPS curve deconvolution

Sample	Vanadium	Tin	Oxygen ($O_2^{-defect}$)
$Sn_{0.675}V_{0.343}O_2$ (Formula unit from Rietveld refinement)	V $2p_{1/2}$:520.5 V^{3+} $2p_{3/2}$: 65.0 V^{4+} $2p_{3/2}$:918.8 V^{5+} $2p_{3/2}$:1132.0	Sn^{4+} $3d_{3/2}$:17426.1 $3d_{5/2}$:24923.3	O 1s: 6730
$Sn_{0.696}V_{0.304}O_2$	V $2p_{1/2}$:605.4 V^{3+} $2p_{3/2}$:122.8 V^{4+} $2p_{3/2}$:1005.5 V^{5+} $2p_{3/2}$:1248.3	Sn^{4+} $3d_{3/2}$:26310.1 $3d_{5/2}$:18139.3	O 1s: 6975

Step 2: *Normalization of areas calculated by photoelectron scattering cross section of respective orbitals.*

The above estimated areas were normalized by photoelectron scattering cross section values of σ_{2p} orbital of V: 0.1308, σ_{3d} orbital of Sn: 0.3442 (for Al k_α radiation). Finally, the vanadium content per formula unit obtained from Rietveld refinement was resolved in terms of co-existence of V^{3+}, V^{4+} and V^{5+} states:

Table 2: Surface electronic composition based on XPS and refinement results

Sample	SnO_2	$Sn_{0.696}V_{0.304}O_2$	$Sn_{0.657}V_{0.343}O_2$
V^{3+} relative%	-	5.2% of 30.4%=1.580	3% of 34.3%=1.029
V^{4+} relative%	-	42.3% of 30.4%=12.859	43.5% of 34.3%=14.920
V^{5+} relative%	-	52.5% of 30.4%=15.96	53.5% of 34.3%=18.350
Quantitative oxidation states of metal atoms as per XPS	Sn^{4+}	$Sn^{4+}_{0.696}V^{3+}_{0.016}V^{4+}_{0.128}V^{5+}_{0.160}$	$Sn^{4+}_{0.657}V^{3+}_{0.010}V^{4+}_{0.150}V^{5+}_{0.183}$

Step 3: *Final surface charge estimation*

Finally, based on the surface composition per formula unit, the net charge content is calculated:

Table 3: Net excess surface charge calculation

Sample	SnO_2	$Sn_{.696}V_{0.3040}O_2$	$Sn_{0.657}V_{0.343}O_2$
Additional positive charge of metal atoms due to V doping	-	$[(4\times0.696)+(3\times0.016)+(4\times0.128)+(5\times0.160)]-(2\times2)=0.144$	$[(4\times0.657)+(3\times0.010)+(4\times0.150)+(5\times0.183)]-(2\times2)=0.173$

Since both the vanadium doped samples have comparable surface oxygen vacancy (as obtained from XPS), the overall surface charge was determined by the relative ionic states of V and Sn atoms. $Sn_{.696}V_{0.304}O_2$ having ~1.2 times lesser additional surface positive charge than $Sn_{0.657}V_{0.343}O_2$ shows 1.2 times better ammonia sensing than latter. This can be attributed to lesser surface electron immobilization in $Sn_{.696}V_{0.304}O_2$ than $Sn_{0.657}V_{0.343}O_2$, therefore leading to greater electron flow to bulk(see ref. 48 of main paper). .

Case 2: Al doped SnO_2 nano systems with oxygen vacancies (Sl. No. 1 of Table 1 in main paper)

Table 4: Quantitative values of area under curve obtained from XPS curve deconvolution

Sample	Aluminium	Tin	Oxygen ($O_2^{-defect}$)
$Sn_{0.947}Al_{0.144}O_{1.881}$ (Formula unit from Rietveld refinement)	Al 2p: 140.55 (Al^{3+}) 22.432 (Al^{2+})	Sn 3d: 36217	O_2^{defect}: 6095
$Sn_{0.869}Al_{0.242}O_{1.888}$	Al 2p: 581.47 (Al^{3+}) 74.51 (Al^{2+})	Sn 3d: 42255	O_2^{defect}: 5594

Table 5: Surface electronic composition based on XPS and refinement results

Sample	Surface electronic composition
$Sn_{0.947}Al_{0.144}O_{1.881}$ (Formula unit from Rietveld refinement)	$Sn_{0.947}^{4+}Al_{0.020}^{2+}Al_{0.124}^{3+}O_{1.881}^{2-}$
$Sn_{0.869}Al_{0.242}O_{1.888}$	$Sn^{4+}_{0.869}Al^{2+}_{0.027}Al^{3+}_{0.215}O_{1.888}^{2}$

Table 6: Net excess surface charge calculation

Sample	Surface positive charge/formula unit
$Sn_{0.947}Al_{0.144}O_{1.881}$	$[(4\times0.947)+(2\times0.020)+(3\times0.124)-$

(Formula unit from Rietveld refinement)	$(2 \times 1.881)] = 0.438$
$Sn_{0.869}Al_{0.242}O_{1.888}$	$[(4 \times 0.869) + (2 \times 0.027) + (3 \times 0.215) - (2 \times 1.888)] = 0.399$

For Al doped SnO_2 nano systems, contribution from surface oxygen vacancy in each sample was included in overall surface charge calculation which showed that $Sn_{0.947}Al_{0.144}O_{1.881}$ and $Sn_{0.869}Al_{0.242}O_{1.888}$ have excess surface positive charge/formula unit with values 0.438 and 0.399 respectively. Due to lesser surface electron mobilization in latter, the $Sn_{0.869}Al_{0.242}O_{1.888}$ sample is more responsive to reducing ethanol gas than the former (see ref. 47 of main paper).