Supplementary Information

Dopant induced cationic bivalency in hierarchical antimony doped tin oxide nano-particles for room temperature SO_2 sensing

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Sample preparation for ICP spectroscopy

For ICP spectroscopic studies, powder samples were initially dissolved in hot conc. HCl. The aim of performing ICP analysis of powder samples was to investigate the molar ratio of Sb:Sn since it was difficult to analyze composition from Rietveld refinement due to similar scattering factors of Sb^{3+} and Sn^{4+} ions. For sample preparation, 0.1 g of powder sample was dissolved completely in 20 cc HCl. The Sb:Sn ratio obtained was used to fixed the composition during Rietveld refinement.

Table S1: Relative area under the deconvoluted XPS curves.

Sample	tin	antimony	oxygen
$Sn_{0.957}Sb_{0.043}O_2$	Sn^{4+}: 35637 Sn^{2+}: 24510	Sb^{3+}: 15344	O^{2-}: 13321
$Sn_{0.856}Sb_{0.144}O_2$	Sn^{4+}: 20585 Sn^{2+}: 32991	Sb^{3+}: 25450	O^{2-}: 11737

Table S2: Value of Hall Coefficients for $Sn_{0.856}Sb_{0.144}O_2$ at different temperatures.

Temperatures (°C)	Hall Coefficient (cm^3 $coulomb^{-1}$)
10	-1.1880×10^{-7}
20	-1.1797×10^{-7}
30	-1.1786×10^{-7}
50	-1.2015×10^{-7}
70	-1.0318×10^{-7}

Table S3: Particle size and interplanar distance calculated from TEM.

Sample	Particle size (nm)	Interplanar (110) distance (Å) from TEM	Interplanar distance (110) (Å) from XRD
$Sn_{0.936}O_2$	18	3.4069	3.4071
$Sn_{0.957}Sb_{0.043}O_2$	14	3.4266	3.4254
$Sn_{0.856}Sb_{0.144}O_2$	17	3.4140	3.4134

Table S4: Values of the topographical properties for pure and antimony doped tin oxide sensors.

Sample	$Sn_{0.936}O_2$	$Sn_{0.957}Sb_{0.043}O_2$	$Sn_{0.856}Sb_{0.144}O_2$
Arithmetic mean height (Sa)	17.985 µm	27.752 µm	20.828 µm

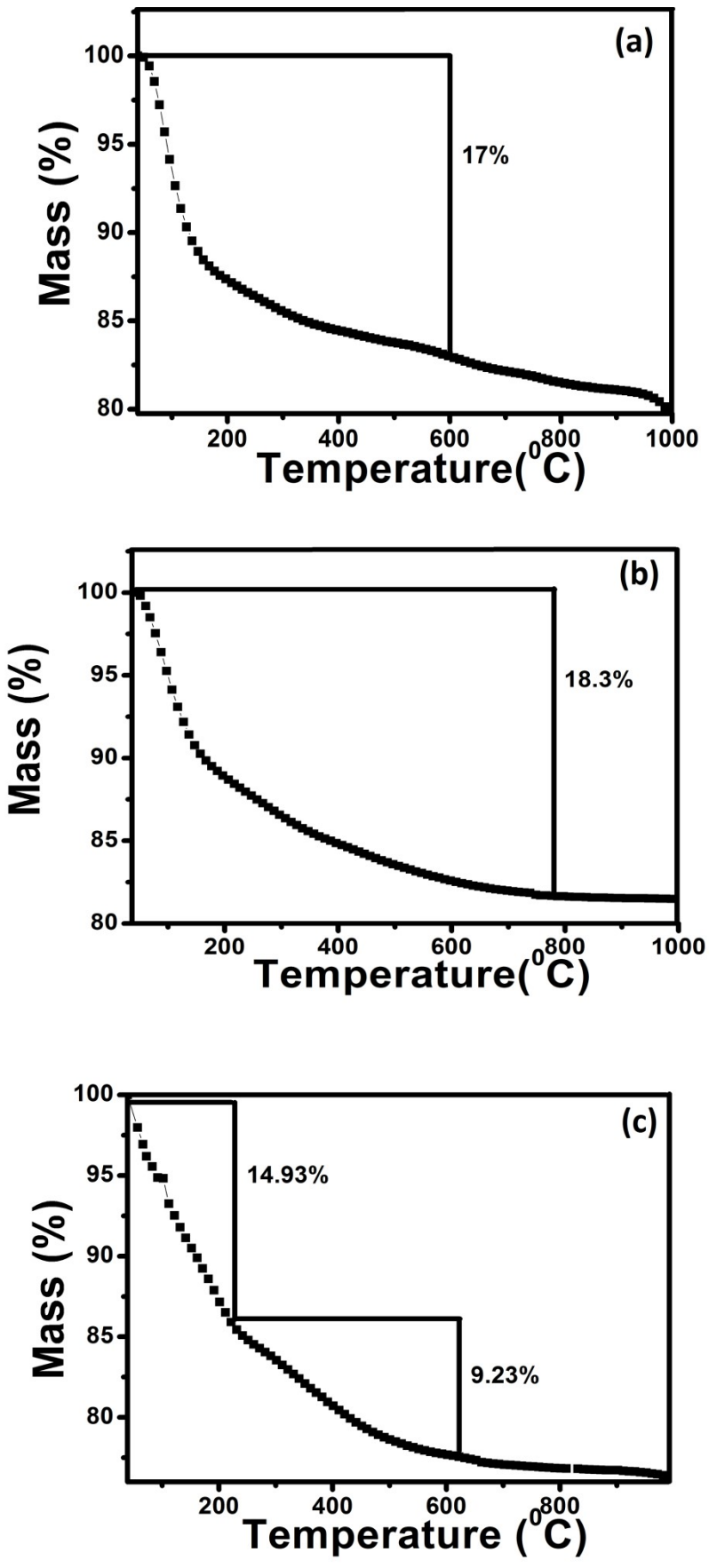

Fig S1: TGA plots of (a) $Sn_{0.936}O_2$ (b) $Sn_{0.957}Sb_{0.043}O_2$ and (c) $Sn_{0.856}Sb_{0.144}O_2$ respectively

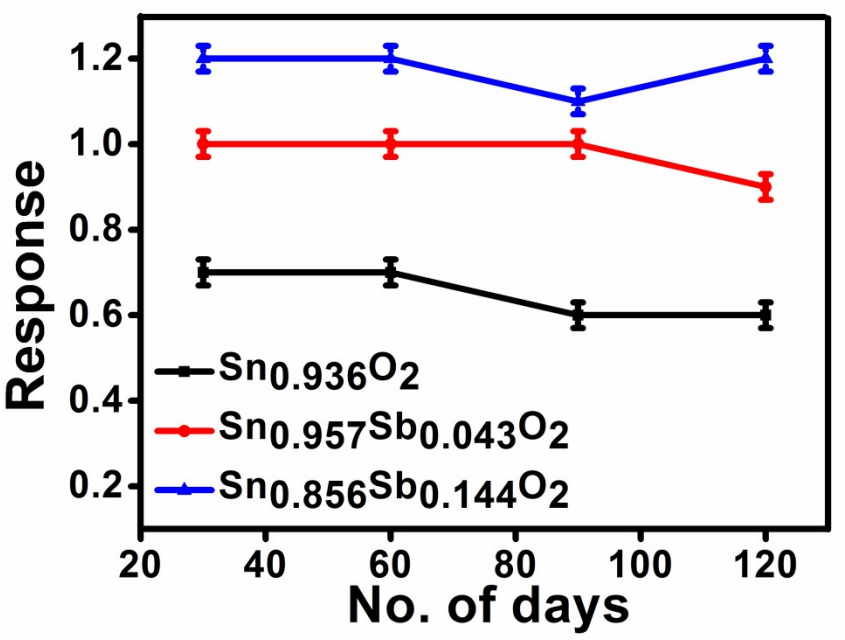

Fig S2: Stability analysis of the antimony doped tin oxide sensors for 120 days. The uncertainty is represented as error bars.

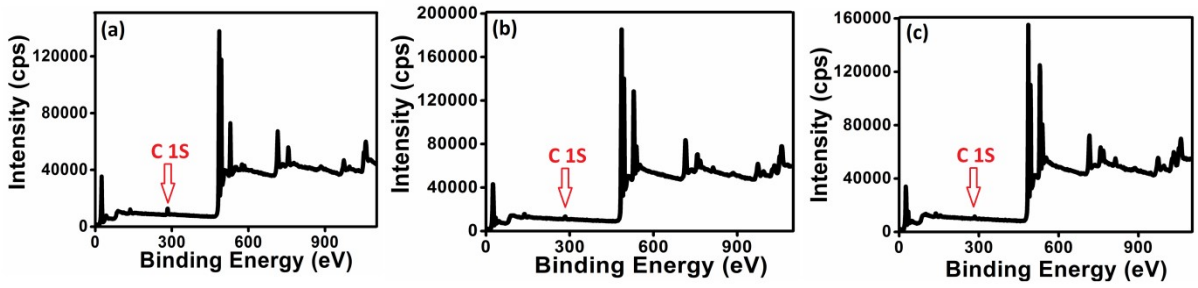

Fig S3: XPS survey scan of (a) $Sn_{0.936}O_2$ (b) $Sn_{0.957}Sb_{0.043}O_2$ and (c) $Sn_{0.856}Sb_{0.144}O_2$.

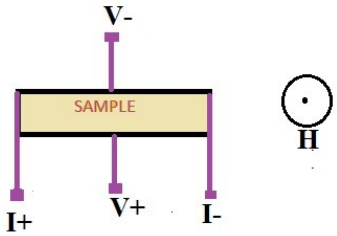

Fig S4: Experimental set-up for measurement of Hall Effect in $Sn_{0.856}Sb_{0.144}O_2$. V stands for voltage, I stands for current and H for magnetic field.

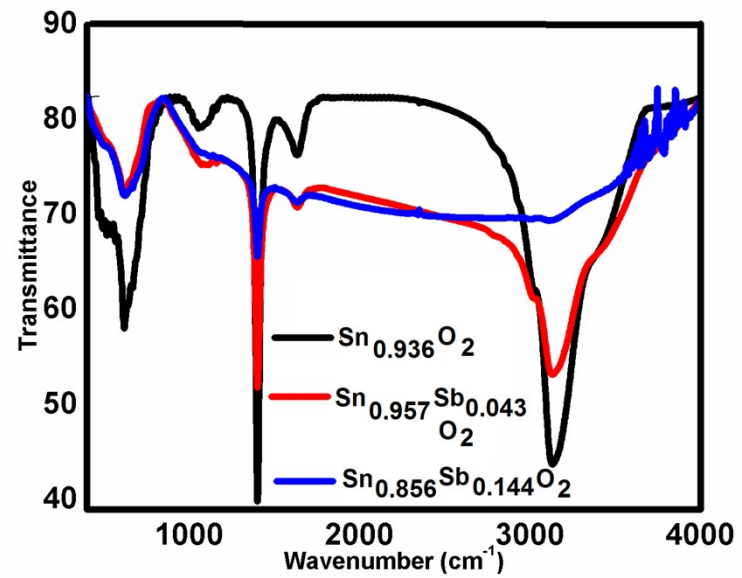

Fig S5: FTIR spectra of (a) $Sn_{0.936}O_2$ (b) $Sn_{0.957}Sb_{0.043}O_2$ and (c) $Sn_{0.856}Sb_{0.144}O_2$ respectively.

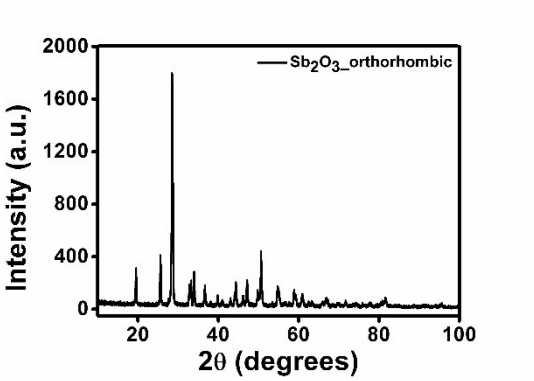

Fig S6: Powder X-ray diffraction pattern of Sb_2O_3 (orthorhombic) phase material using Cu K_α radiation source.

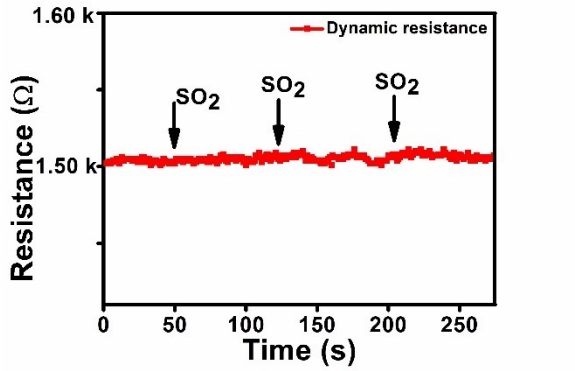

Fig S7: Insensitivity of Sb_2O_3 (orthorhombic) sensor to pulses of SO_2 gas (2 ppm).

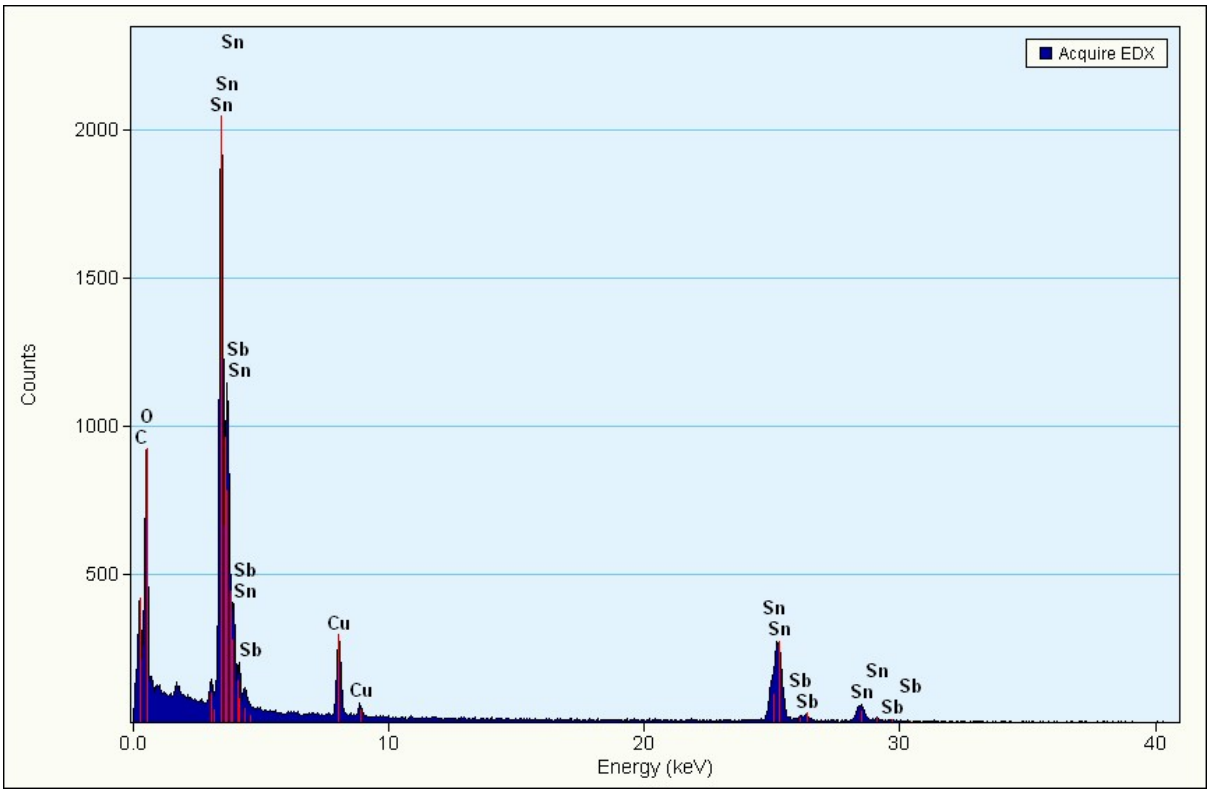

Fig S8: EDX spectrum of $Sn_{0.957}Sb_{0.043}O_2$ sample. Signals of Cu and C are due to use of copper coated carbon grids during TEM.

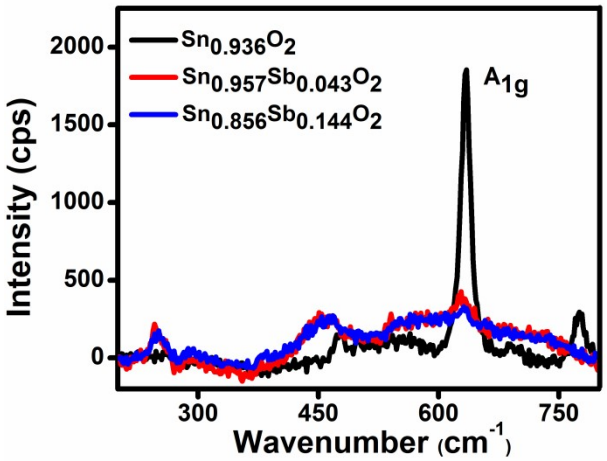

Fig S9: Room temperature Raman spectra of pure and antimony doped tin oxide samples. The shifting of A_{1g} vibration mode (indicative of tin vibrations) towards lower wave number region in doped samples indicates doping of Sn^{4+} by a species of larger ionic radius like Sb^{3+} and elongation of Sn-O bond in doped samples.

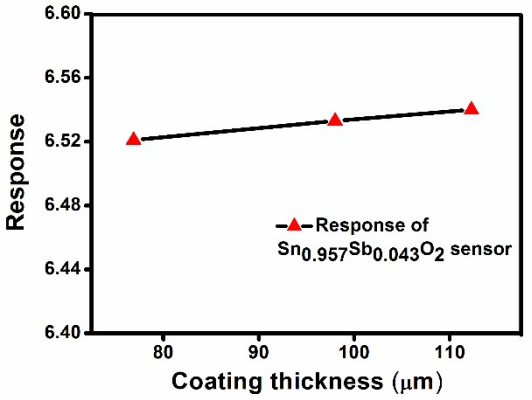

Fig S10: Plot of sensing response to 2 ppm SO_2 at room temperature vs. variation in sensor coating thickness for $Sn_{0.957}Sb_{0.043}O_2$ sample. Over a range of 70-120 μm, the response change is negligible.