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X-RAY PHOTOEMISSION SPECTROSCOPY (XPS) ANALYSIS ON PLATINUM DOPED STANNIC OXIDE CERAMIC

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ABSTRACT

Pt-SnO_2 ceramics were fabricated by the dry pressing method and sintered at 1000^oC. The XPS spectrum showed the Sn 4d, Sn 4p, Sn 4s, C 1s,Sn $3d_{5/2,}$ Sn $3d_{3/2,}$ O 1s, Sn $3p_{1/2}$ and Sn 3s peaks. The high resolution scan of revealed that the O 1s has a binding energy of 530.2 eV which indicates that there were oxygen vacancies in the doped material. The FWHM XPS spectrum was broader than the pure SnO_2, which shows that there is a greater range of chemical environments and hence binding energies. The asymmetry in the O 1s also shows that adsorbed oxygen exists on the surface of the sample in ambient atmosphere. The Sn $3d_{5/2}$ peak was symmetric and has a small FWHM indicating that the compound has one component only. The atomic ratio of oxygen and tin (ratio of O 1s and Sn $3d_{5/2}$) is ~ 1.30 :1, a deviation of stoichiometry which was caused by oxygen deficiency on the surface region. The binding energies of both the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ shifted by 0.01 eV with respect to the pure SnO_2 XPS spectrum sintered at the same temperature (1000^oC) and this is an indication that the chemical environment was changing due to the incorporation of Pt in SnO_2. The Pt(2) which shows from the XPS spectrum was probably an oxide layer on the Pt metal or possibly dissolved in the SnO_2. The XPS analysis also showed that the Pt 4 f looks like mainly Pt(0) or Pt metal.

INTRODUCTION

X-ray photoemission (XPS) is a technique for surface analysis in which monoenergetic soft X-rays are irradiated on a solid in vacuum and analyzing the emitted electrons by energy. The typical spectrum is a plot of the number of detected electrons per energy interval against their kinetic energy. XPS is a unique surface-sensitive technique for chemical analysis because the mean free path of electrons in solids is very small, thus the detected electrons originate from the first few atomic layers (from the irradiated surface). Data can be obtained from peak heights or peak areas and chemical states identification from exact measurement of peak positions and separations and spectral features. Pt-SnO_2 ceramics at low doping of Pt in SnO_2 were reported to show its optimum composition was 0.5 wt.% Pt in SnO_2 when sintered at 1000^oC and operated at an optimum temperature of 400^oC for sensing methane in air [1]. To understand the

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effect of Pt in SnO_2, X-ray Diffraction method showed a slow and small growth of average mean crystallite size (~ 50 nm) with increasing Pt [2] but does not explain the high sensitivity towards methane in air. The work reported here is based on the X-ray Photoemission Spectroscopy (XPS) study on the doped Pt-SnO_2 ceramic which may offer explanation for the high sensitivity observed.

EXPERIMENTAL PROCEDURES

Dry pressing ceramics preparations
Powdered SnO_2 supplied by Fluka and powdered platinum supplied by Aldrich were mixed mechanically with nominal compositions of SnO_2(100-x)Pt(x), with x in weight % with x = 0 and x = 3. The total mass of the mixtures was approximately 10 g. The mixtures were dry-pressed using pressure of 40 MPa for five minutes. The green-body of the formed ceramics was in a form of circular disc with a diameter of 40 mm and a thickness of 2 mm. The samples were sintered in an electrical furnace (CARBOLITE) at a temperature of 1000ºC for 1 hour at a rate of 20^{o}C per minute. Each sample was sintered separately as to avoid contamination.

XPS
XPS data was acquired using the Scienta ESCA 300 X-ray photoelectron spectrometer at the RUSTI facility at the Daresbury Laboratory, Warrington, United Kingdom. About 0.5 g of the powdered samples were used and filled in a cavity about the same level as the stub. A monochromated Al K_{α} source ($h\upsilon$ = 1486.6 eV) was used in conjunction with the 300 mm radius concentric hemispherical analyser and the acquisition parameters were typically 150 eV pass energy, 0.5 mm entrance slit size and 0.05 eV incremental step size. The absolute binding energies of the photoelectron spectra were determined by referencing to the C1s transition at 284.6 eV which resulted from background hydrocarbons from the ultra-high-vacuum environment. The O 1s, Pt 4f and Sn 3d were taken before and after all region scans and the shape and intensity were consistent to approximately 1% and the binding energies were reproducible to within ± 0.05 eV.

RESULTS AND DISCUSSIONS

The XPS survey spectrum of the 3 wt.% Pt-SnO_2 sintered at 1000^{o}C is shown in Figure 1. The spectrum have all been referenced to a C 1s binding energy value of 284.6 eV. The XPS spectrum shows the Sn 4d, Sn 4p, Sn 4s, C 1s, Sn $3d_{5/2,}$ Sn $3d_{3/2,}$ O 1s, Sn $3p_{1/2}$, Sn 3s. A closer look at the O 1s as in Figure 2 revealed that the binding energy was 530.2 eV which is lower than the expected value 530.6 eV. This lower value indicates that there were oxygen vacancies in the doped material. The FWHM of the doped (3 wt.% Pt-SnO_2) XPS spectrum is broader than the undoped case, which shows that there is a greater range of environments and hence binding energies. The symmetry in the O 1s also shows that adsorbed oxygen exists on the surface of the sample in ambient atmosphere [3].

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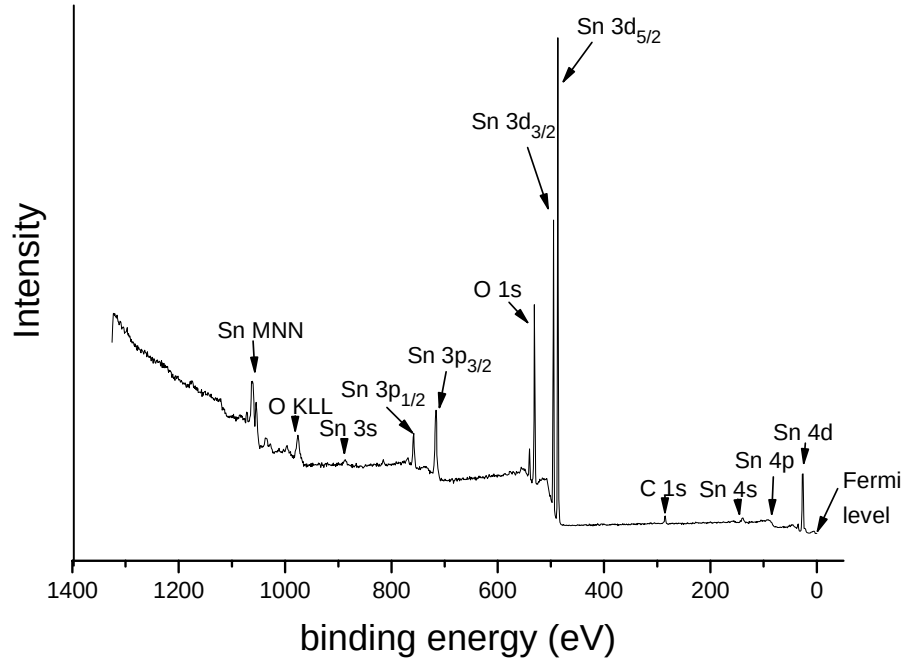

Figure 1: XPS survey spectrum of the 3 wt.% Pt-SnO_2 sintered at 1000°C.

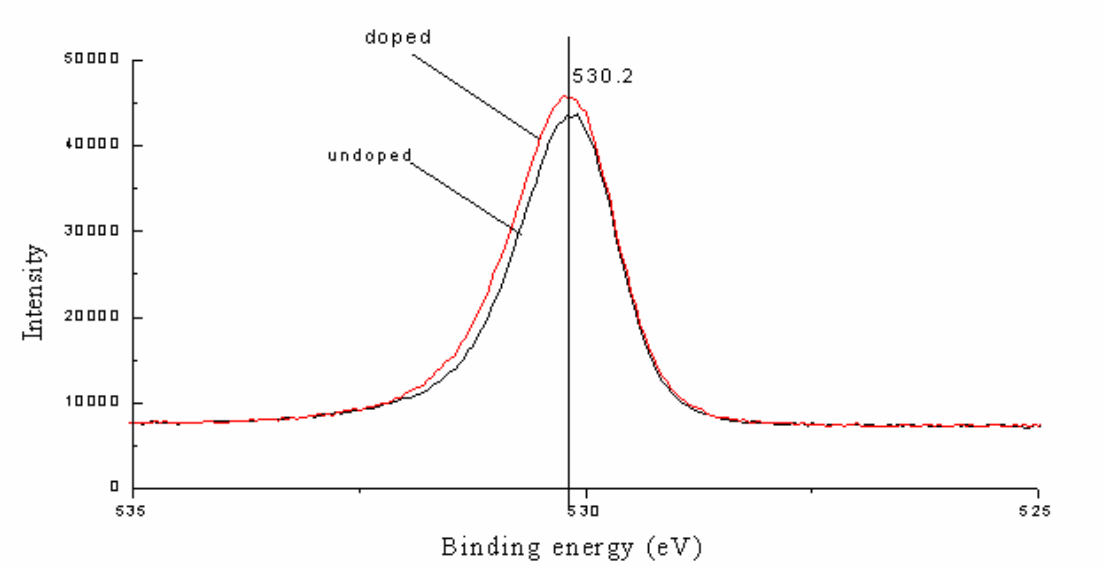

Figure 2: O 1s of doped (3 wt.% Pt) and undoped (SnO_2) sintered at 1000°C.

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The Sn $3d_{5/2}$ and Sn $3d_{3/2}$ XPS spectrum is replotted as in Figure 3. The Sn $3d_{5/2}$ has a binding energy of 486.2 eV and the binding energy of the Sn $3d_{3/2}$ was 494.2 eV which is in agreement with other data [4]. The separation between the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ is 8 eV which is smaller than the value reported by Yoo et al. [5].

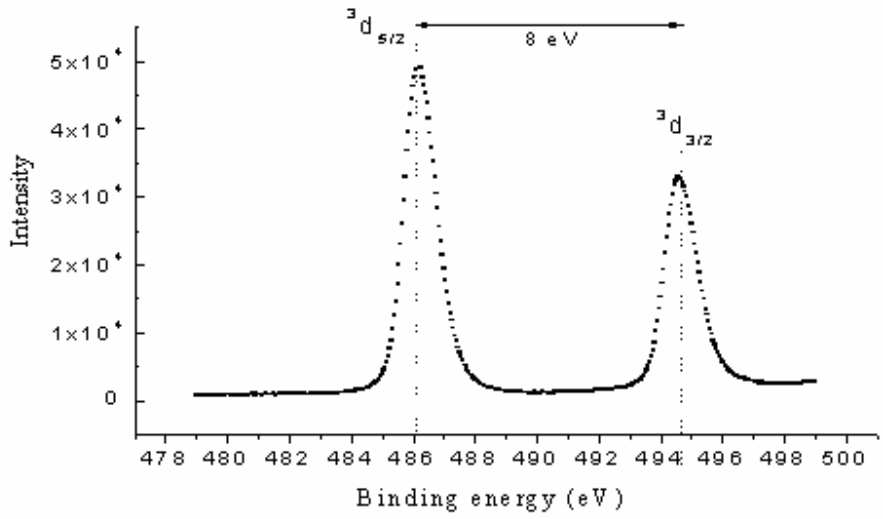

Figure 3: $3d_{5/2}$ and $3d_{3/2}$ of the 3 wt.% Pt-SnO_2 dry-pressed ceramics sintered at 1000°C.

A closer look at the Sn $3d_{5/2}$ shows only one symmetry (with no shoulder peak) and a small FWHM indicating that the compound has one component only. The atomic ratio of oxygen and tin (ratio of O 1s and Sn $3d_{5/2}$) is ~ 1.30 :1, a deviation of stoichiometry which was caused by oxygen deficiency on the surface region. Notably, the XPS is based on the photoelectric effect and the X-ray penetration is fairly low which gives information up to a depth of ~ 20 Å from the surface of the sample. The binding energies of both the Sn $3d_{5/2}$ and Sn $3d_{3/2}$ shifted by 0.01 eV w.r.t the pure SnO_2 XPS spectrum sintered at the same temperature (1000°C) and this is an indication that the chemical environment was changing [6] due to the incorporation of Pt in SnO_2. The Pt 4 f XPS spectrum is shown in Figure 4. The Pt(0) or Pt $4f_{7/2}$ has a centre of gravity at ~ 71.17 and 74.63 eV respectively and the Pt(2) or $4f_{5/2}$ has a centre of gravity at ~ 72.38 and binding energy of 75.82 eV.

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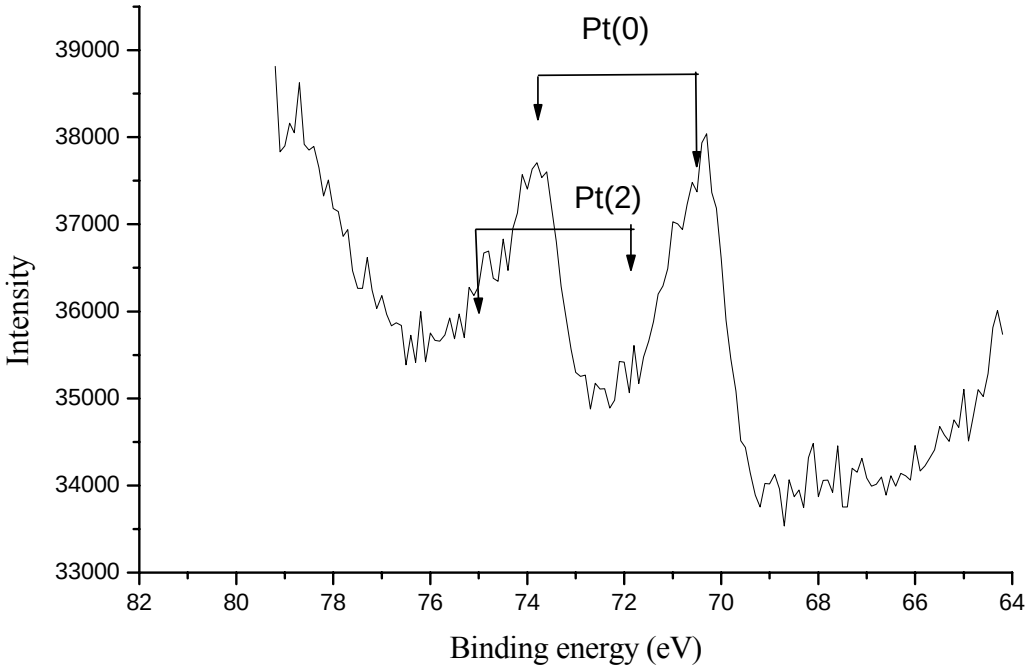

Figure 4: Pt 4f $_{7/2}$ and $4f_{5/2}$ of 3 wt.% Pt-SnO_2 dry-pressed ceramics sintered at 1000^{o}C.

This intensity ratio Pt 4f $_{7/2}$: $4f_{5/2}$ was found to be 1.29: 1.38 as in Figure 5. This result is in good agreement with Fildman and Mayer and Lee and Chung [7,8]. This photoemission from the f electronic states produces a spin-orbit doublet which is the Pt $4f_{7/2}$ - $4f_{5/2}$ lines. High resolution XRD only shows the Pt(0) states but not Pt(2) [9]. The Pt(2) which shows from the XPS spectrum were probably an oxide layer on the Pt metal or possibly dissolved in the SnO_2. However, the XPS analysis above showed that the Pt 4 f looks like mainly Pt(0) or Pt metal. This is further supported by the fact that Pt oxidation is known to be highly passivating [10] and that platinum oxide, PtO_2 which are relatively stable oxide of platinum was confined to particle sizes < 0.75 nm [10] and temperature below 875 K [11]. None of the reported TEM work show such sizes even at room temperature nor in the ceramics that were sintered at 1000^{o}C [12].

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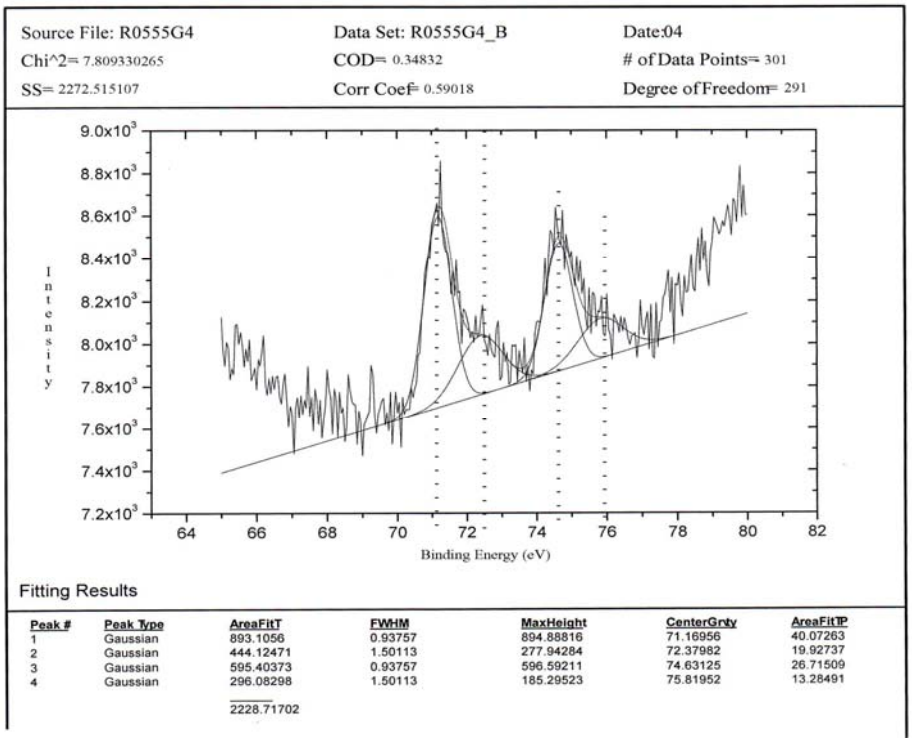

Figure 5: Peak ratio Pt $4f_{7/2}$ and $4f_{5/2}$ of 3 wt.% Pt-SnO_2 dry-pressed ceramics sintered at 1000°C.

The XPS valance band of pure and doped SnO_2 is shown in Figure 6. The introduction of 3 wt. % Pt has modified the valance band top edge. A band of surface states which are energetically located inside the modified ceramic are associated with the Pt incorporation. Altman and Gorte [14] and Henshaw et al. [15] reported similar bands in an additive-modified oxide semiconductor in their XPS and UPS analysis. In their case, the band of surface states are directly associated to the additive presence whilst in another case it was an indirect association with the additive presence [16]. In the case of SnO_2, a surface band state was observed in sputtered tin oxide surfaces. The bridging oxygen ions have been removed which give rise to a local SnO-like configuration.

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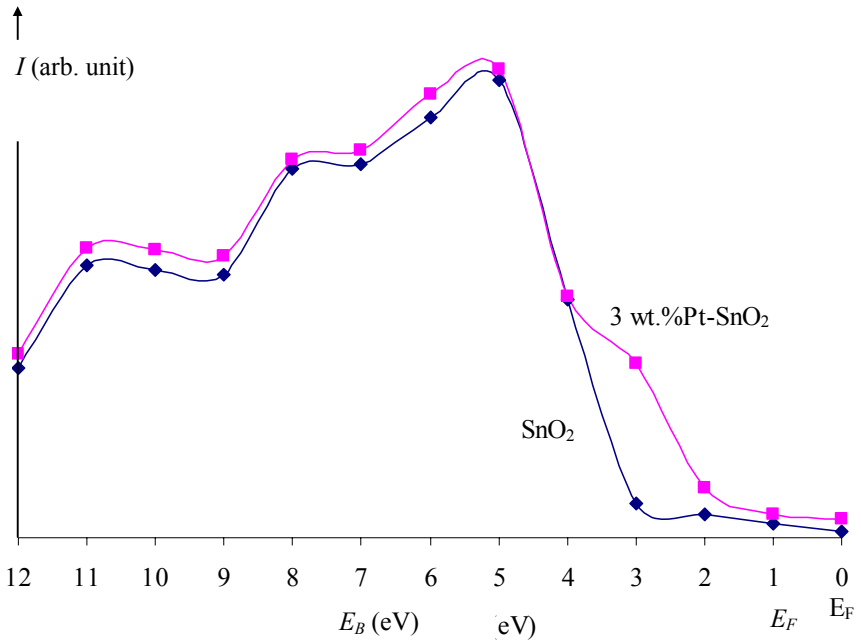

Figure 6: XPS valance band of the pure and doped SnO_2 sintered at 1000°C.

The introduction of Pt introduce a higher density of states between the Fermi level E_F and the valence band. E_B is the binding energy and E_F is the Fermi energy.
Which is the source of the new valence states [17,18]. When SnO_2 was exposed to CH_4, Kawabe *et al.* found that the Sn^{2+} associated bands increased [19]. Thus, the evolution of the total density of the mentioned surface states was identical to that of the Pt chemical state concentrations. The band could arise from Pt^{+2} ions at the outermost layers of the Pt localised in the surface of the modified tin oxide crystallite which was observed and mentioned earlier.

CONCLUSION

From the XPS analysis, the high sensitivity of the Pt-SnO_2 ceramic towards methane is attributed to the presence of oxygen vacancies and greater range of chemical environments which may enhances spill over mechanism. This in turn will cause a great difference of conductance in air and in methane, thus accounting for the high sensitivity in such material. This is further supported by the stability of Pt incorporated in the ceramic.

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