**Chemochromic Pd-V2O5 Sensors for Passive Hydrogen Detection in
Nuclear Containments – 18268**

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ABSTRACT

The ability to detect and monitor hydrogen gas efficiently in process and storage facilities, handling nuclear material, is crucial to ensuring their safety. The accumulation of hydrogen gas, above the lower flammable limit (LFL), in a nuclear waste containment is a concern since it creates the potential for a hydrogen-air explosion to occur, which could lead to a loss of containment and result in the uncontrolled release of radioactive material into the surrounding environment. The events that took place at Fukushima Daiichi Nuclear Power Plant highlighted the vulnerability of conventional hydrogen detection to extreme events, where power may be lost. In the present work, chemochromic hydrogen sensors have been fabricated, using transition metal oxide thin films, to provide eye-readable detection systems that would be resilient to plant power failure. Vanadium oxide (V_2O_5) films were prepared on quartz glass substrates by sol-gel deposition and sensitized with a palladium (Pd) catalyst, deposited by electron beam evaporation. When exposed to hydrogen, the Pd catalyst dissociates H_2 to H atoms, which diffuse into the $V^{(V)}_2O_5$ forming a hydrogen-vanadium metal bronze, $H_2V^{(III)}_2O_5$, resulting in a noticeable colour change from orange to dark green. To assess their viability for nuclear safety applications, these sensors have been irradiated to total doses between 5 and 250 kGy using a Co-60 gamma isotope irradiator. The results suggest that gamma irradiation, at the levels examined, has an effect on the initial colour of the V_2O_5 and Pd-V_2O_5 thin films with decreased transmittance above 540 nm. The orange starting colour darkened and developed a green tone, with the degree of colour change depending on the applied total dose. Changes in surface morphology and characteristics have been examined by using Scanning Electron Microscopy (SEM) and Raman spectroscopy. High level (250 kGy) gamma radiation exposure begins to produce surface degradation on V_2O_5 thin films; however this behaviour is not observed for films that are also coated with palladium. Chemochromic properties of both un-irradiated and irradiated Pd-V_2O_5 thin films were determined by examining their optical transmittance, using UV-vis spectroscopy, under exposure to a 4% H_2-N_2 gas mixture. Exposure to gamma radiation has been found to have negligible effect upon colour change behaviour after 30 minutes exposure to hydrogen gas. The results suggest that the thin film V_2O_5 sensitised with Pd is a plausible technique for application in the monitoring of hydrogen gas in low-level gamma radiation environments.

INTRODUCTION

Following the Tohoku earthquake in Japan and the subsequent events that occurred at the Fukushima Daiichi Nuclear Plant, whereby hydrogen explosions resulted in severe damage to containment structures and facilities, the resilience of hydrogen management systems to extreme events has been of high interest. Hydrogen management systems on nuclear plants are typically designed to maintain the hydrogen concentration significantly below the lower flammability limit (LFL) of 4 %, by systems such as venting. However, in extreme circumstances, primary hydrogen management and detection systems may fail leaving the facility vulnerable to hydrogen build up and consequent risk of explosion.

Hydrogen gas is intrinsic to many process and storage facilities handling nuclear material and can be released under both normal operations and accident conditions.

There are two main sources of this hydrogen: radiolysis of water or organic materials; and corrosion of metals (generally magnesium, zirconium and uranium).

Monitoring the hydrogen concentration is; essential in ensuring the safety of a nuclear containment and indicates any severe or sudden increases in hydrogen concentration. Traditional hydrogen detection methods include gas chromatographs, mass spectrometers or ionisation gas pressure sensors. These instruments are expensive, relatively large, time consuming to operate and require sampling of gas separate to testing. Hence smaller, faster and cheaper sensors have been developed that can be used in-situ or as portable detection devices. These commercially available sensors rely on an electrical supply to produce a hydrogen concentration measurement and therefore provide no measurements when power supply is lost. However, certain transition metal oxides have chemochromic properties and so have the potential to be used as passive visual indicators for the presence of hydrogen, and be resilient to power failures that might occur following extreme events. [1-3]

When hydrogen interacts with certain materials, such as chemochromic metal oxides, their optical properties change. Colour change in the visible region is attributed to the progressive reduction (change in oxidation state) of the metal ions, due to the double injection of electrons and H^+ ions into the MO_x layer, forming hydrogen metal bronzes H_yMO_x resulting in a chemochromic change. [4] Equation 1 shows a general formula for this reaction:

$$MO_x + yH^+ + ze^- \leftrightarrow H_yMO_x \qquad\qquad \text{(Eq. 1)}$$

This phenomenon can be exploited for the detection of hydrogen. [2] Metal oxides such as vanadium oxide (V_2O_5), molybdenum oxide (MoO_3) and tungsten oxide (WO_3) are commonly used due to their: high chemical stability, layer-like structures with gas storage ability, relative low costs, easy preparation methods and comparatively low toxicity. [5, 6]

The majority of the developed chemochromic hydrogen sensors have been designed to operate in non-radioactive conditions. In order to use such sensors on nuclear plant, there is therefore a need to characterise the effect of ionising radiation exposure upon their behaviour. Van Duy et al. [1] studied the effect of gamma irradiation on the hydrogen gas-sensing characteristics of Pd-SnO_2 thin films. The sensitivity of the sensor was seen to increase sizably with increasing gamma ray dosage from 1 kGy to 100 kGy. It was demonstrated that the enhanced sensing characteristics were due to the formation of an oxygen defect in the metal oxide structure. Shen et al. [7] explored the effects of different levels of irradiation on the transmittance in the visible region of tungsten oxide glasses. At low values (<1 kGy) a negligible difference is seen. When the levels are increased to 7 kGy the transmittance is halved which would significantly affect the sensitivity and accuracy of a tungsten oxide hydrogen sensor. It is suggested that, in the case of tungsten oxide, gamma irradiation can convert W^{6+} to W^{5+} or W^{4+} which is the same response as seen in a hydrogen atmosphere. Vasanth-Raj et al. [8] and Ezz-Eldin [9] found similar responses for V_2O_5-P_2O_5 glasses and TiO_2 respectively. Both postulated that the presence of lower valence state metal ions is expected to increase due to radiation exposure according to possible photochemical reduction of the metal ions shown in equation 2. [9]
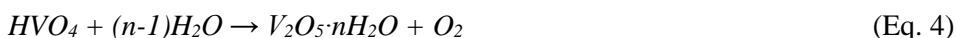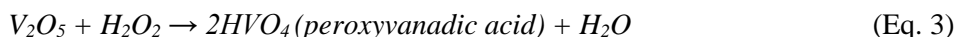
$$M^{x+} + ye^- \rightarrow M^{(x-y)+} \qquad\qquad \text{(Eq. 2)}$$

However, Bello-Lamo et al. [10] show that the radiation above 30 kGy has no effect on the inner crystal structure of TiO_2 and the small changes on the surface layer only result in a relatively low (<5 %) reduction in transmittance. Hence previous studies into the effect of gamma irradiation on transition metal oxides are divided. Currently there is no detailed study in literature about the effect of gamma irradiation on the hydrogen sensing behaviour of vanadium oxide thin films prepared by sol-gel. Hence, the present investigation was carried out to characterise said effects on Pd-V_2O_5 thin films.

The Pd-V_2O_5 thin film samples were irradiated with gamma rays to a variety of total doses, ranging from 5 kGy up to 250 kGy. Sensing performance was measured post irradiation via a UV-Vis spectrophotometer.

EXPERIMENTAL

Preparation of V_2O_5 coatings

Vanadium pentoxide, V_2O_5, thin films were deposited on quartz coated glass substrates by spin coating using an inorganic sol-gel precursor. 0.5 g V_2O_5 powder (99.5 %) was dissolved in 30 ml of 15 % H_2O_2 solution. The reaction is exothermic so H_2O_2 was added drop wise with vigorous stirring. Once dissolved the clear orange solution was heated at 70 °C for 1 hour in air. After 10-15 minutes oxygen is vigorously evolved due to the decomposition of excess H_2O_2. At the same time the solution turns dark red and is transformed into a viscous homogeneous solution of $V_2O_5 \cdot nH_2O$ hydrogels. [6, 7, 9] The reaction mechanisms are as follows according to Ren et al. [11]:

$$V_2O_5 + H_2O_2 \rightarrow 2HVO_4\,(peroxyvanadic\ acid) + H_2O \qquad\qquad (Eq.\ 3)$$

$$HVO_4 + (n\text{-}1)H_2O \rightarrow V_2O_5 \cdot nH_2O + O_2 \qquad\qquad (Eq.\ 4)$$

Prior to deposition, quartz glass substrates (25 mm x 25 mm x 1 mm) were cleaned using an acid 'piranha' solution: a 3:1 mixture of concentrated sulphuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2), rinsed thoroughly with DI water and dried under nitrogen flow. The synthesised $V_2O_5 \cdot nH_2O$ aqueous sol-gel was deposited by spin-coating at 2000 rpm for 30 seconds. Samples were dried in air by infrared lamp at 150 °C for 30 minutes followed by annealing at 350 °C for 1 hour with a ramp rate of 1 °C/min. This process was repeated 5 times to build up the desired film thickness. The resulting films are transparent orange/brown in colour, typical of polycrystalline V_2O_5, with a film thickness of 500 nm ($\pm$ 25 nm) as measured by Dektak 6M stylus profilometer. [10]

Catalyst Deposition

Palladium films with a thickness of ~5 nm were deposited by electron beam evaporation using a Kurt J Lesker PVD 75 with a base pressure of ~4.5x10^{-5} Pa at ambient temperature on to the V_2O_5 thin films. The films were obtained by evaporation of palladium pellets (99.95 %+ purity) at a growth rate of 0.2 Å/sec, deposition rate was observed using a crystal thickness monitor. During each deposition run twelve identical samples were fabricated.

Radiation Exposure

The gamma irradiation exposure experiments were carried out at The University of Manchester's Dalton Cumbrian Facility (DCF) using the Foss Therapy Services Model 812 Cobalt-60 self-shielded irradiator shown in figure 1. [12] V_2O_5 and Pd-V_2O_5 thin films were exposed to gamma irradiation from a Co-60 source at an absorbed dose rate of approximately 200 Gy/min, at room temperature in air atmosphere, to obtain 5 total irradiation doses of 5, 20, 50, 100, 250 kGy. After gamma irradiation the samples were stored at room temperature in a vacuum desiccator, for upto 14 days, until the gas-sensing measurements were performed.

Sample Characterisation

Subsequently the films were analysed using a Renishaw Raman 2000 spectrometer at room temperature using an Ar ion laser with wavelength of 488 nm. The measuring range was $100 - 1200$ cm^{-1}. Surface morphology was characterised with a scanning electron microscope (SEM, FEI Quanta 250).

Fig. 1. Co-60 gamma irradiator.

Hydrogen Gas Sensing

Post-irradiation measurements of the hydrogen sensing characteristics of the thin films were performed using the testing system shown in figure 2. Each sample was placed in a 2.2 L chamber with a fan attachment and hydrogen sensor to ensure a uniform gas composition throughout. For each measurement, the chamber was purged with N_2 prior to injection of 4 vol% H_2/N_2 gas mixture at a flow rate of 5 L/min. The transmission spectra of the thin films were recorded at room temperature using an Ocean Optics Flame-S-UV-NIR spectrometer.
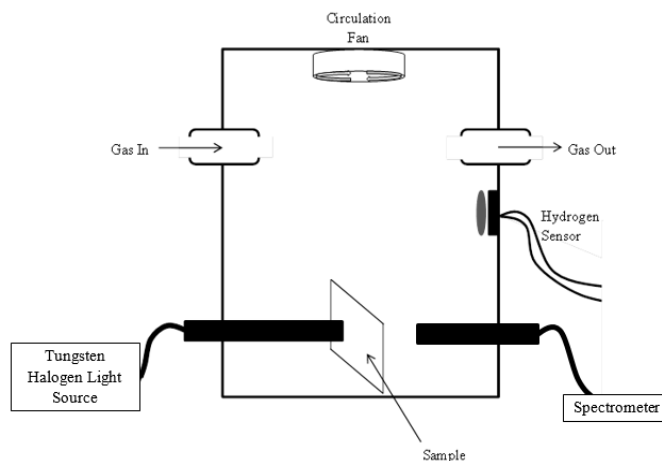

Fig. 2. Schematic of hydrogen gas chamber.

RESULTS AND DISCUSSION

The as manufactured V_2O_5 and Pd-V_2O_5 films are semi-transparent in air. Samples were then irradiated with a Co-60 gamma source to five different total doses of 5, 20, 50, 100 and 250 kGy at room temperature. Visually the samples are seen to darken slightly and the colour appears to change from red-brown to a green-brown colour tone post radiation exposure, the extent of the change seen depends on the applied radiation dose, as seen in figure 3.
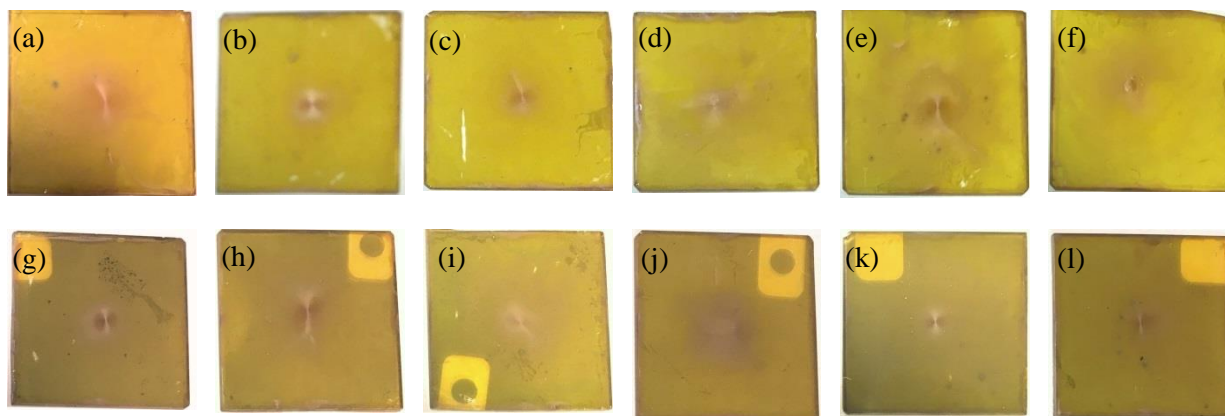

Fig. 3. Images of (a) un-irradiated and the (b) 5 kGy, (c) 20 kGy, (d) 50 kGy (e) 100 kGy and (f) 250 kGy irradiated V_2O_5 thin films. Images of (g) un-irradiated and the (h) 5 kGy, (i) 20 kGy, (j) 50 kGy (k) 100 kGy and (l) 250 kGy irradiated Pd-V_2O_5 thin films.

Structure Characterisation

Raman spectra for the V_2O_5 and Pd-V_2O_5 thin films pre- and post-radiaition are shown in figure 4. There is no characteristic difference between the spectra observed for the V_2O_5 films and those coated with palladium. Palladium lacks distinctive Raman shifts below 1100 cm^{-1} - hence only the effects on V_2O_5 will be discussed. [13]

The structure of crystalline V_2O_5 is a layered structure built from VO_5 square pyramids sharing edges and corners. [14] Within the VO_5 pyramid layers a very short V=O double bond (1.54 Å) is observed as well as four longer (1.8-2.1 Å) V-O bonds making the base of the pyramid. [15] The as prepared films can be assigned to the specific signature of α-V_2O_5 polymorph. [16] The distorted background present on all the spectra could be due to amphorous areas within the V_2O_5 films or the presence of a monoclinic phase VO_2. [17] However, sharp low frequency peaks (below 200 cm^{-1}) suggests that three-dimensional, long-range order is still present in all the films. [18]

Seven characterisitic peaks are seen at 992, 698, 484, 406, 282, 194 and 142 cm^{-1} which agrees with the literature. The high frequency peak at 992 cm^{-1} corresponds to the terminal oxygen (V=O) stretching mode which results from unshared oxygens. The two peaks located at 406 and 282 cm^{-1} are both assigned to the bending vibrations of the V=O bonds. The bridging V-O-V doubly coordinated oxygen results in the bending vibration seen at 484 cm^{-1} and a stretching vibration at 698 cm^{-1}. The intense peak at 142 cm^{-1} and smaller peak at 194 cm^{-1} correspond to lattice vibrations within the layered structure. [17] Two characterisic peaks are missing at 532 cm^{-1} and 309 cm^{-1}, commonly resulting from the stretching and bending of triply coordinated bridging-oxygens respectively. No other peaks representing secondary phases of vanadium and oxygen are observed suggesting a single phase formation. Additionally, the absence of a peak at 850 cm^{-1} indicated that the films are not hydrated (V_2O_5.H_2O), which would typically

be observed as a contaminant. [15] Ezz-Eldin [9] suggests that gamma irradiation results in the reduction of V^{5+} ions to V^{4+} ions. Such a reduction would convert $V^{5+}=O$ bonds to $V^{4+}=O$ and $V^{5+}-O-V^{5+}$ single bonds to $V^{4+}-O-V^{4+}$. However, we do not observe any developing features due to $V^{4+}-O-V^{4+}$ at 750 cm^{-1} or $V^{4+}=O$ at 932 cm^{-1}, suggesting that increased gamma irraditation has little effect on the Raman spectra and the overall V_2O_5 structure. [19]
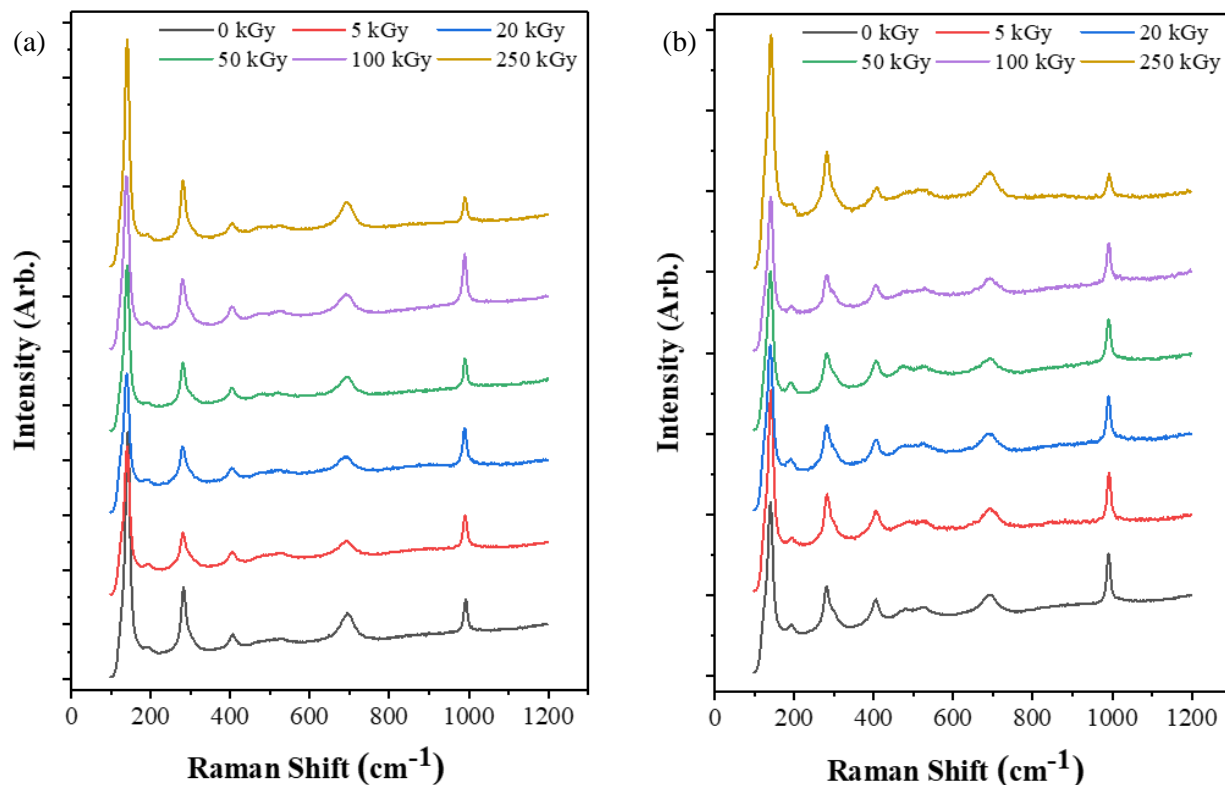

Fig. 4. Raman spectra of un-irradiated and irradiated (a) V_2O_5 and (b) Pd-V_2O_5 thin films.

Morphology

The V_2O_5 and Pd-V_2O_5 thin films with total gamma irradiation doses of 0, 5 and 250 kGy were examined using SEM; the obtained micrographs are shown in figure 5. Fibrous micro reticulated morphology were observed for all the V_2O_5 and Pd-V_2O_5 films. Changes in the film morphology with increased radiation exposure were observed. At 250 kGy absorbed dose, figure 5c., the V_2O_5 thin film show degradation with flaking and the formation of cracks. Deterioration is seen to a smaller extent for the lower total dose, 5 kGy, V_2O_5 thin film (figure 5b.). The effect of radiation on the morphological structure of the Pd-V_2O_5 thin films is much less pronounced (figure 5d-f.). The 5 nm palladium film may be hindering the observation of failure within the V_2O_5 film or acting as a protective coating reducing the susceptibility to failure from radiation exposure. [20]
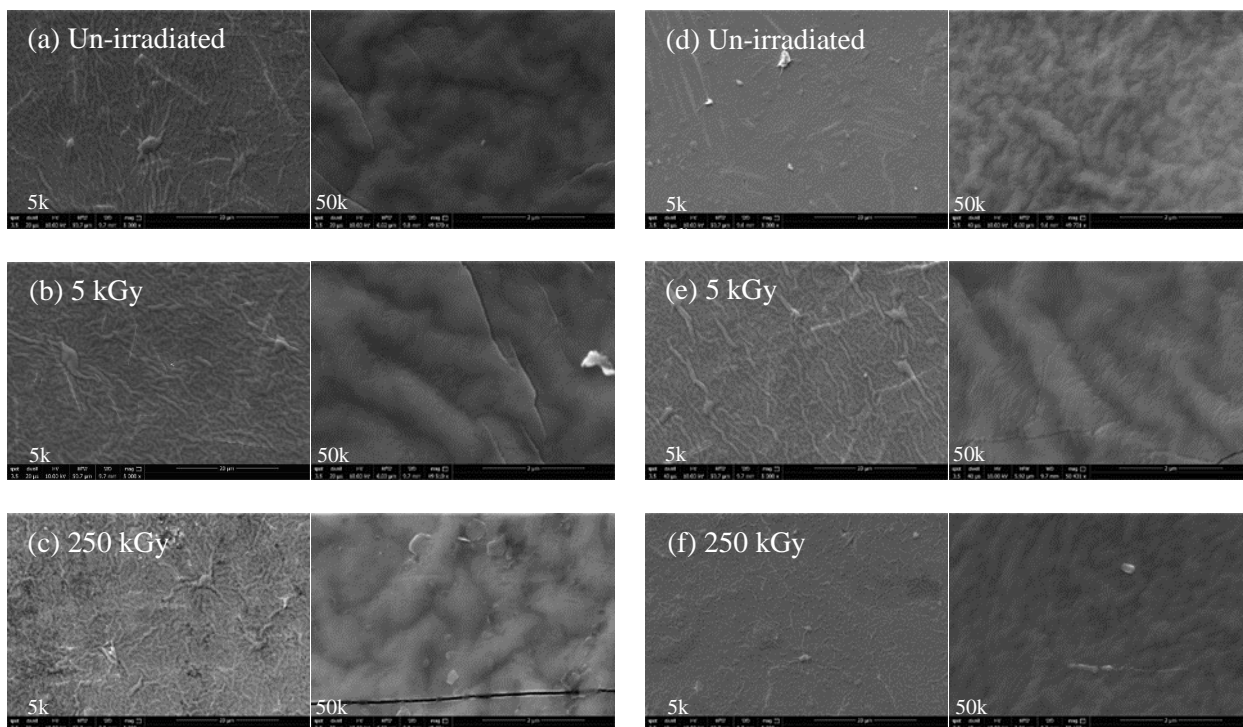
Fig. 5. SEM images at 5k and 50k magnification of V_2O_5 thin films: (a) un-irradiated; and irradiated with dose (b) 5 kGy; and (c) 250 kGy. SEM images at 5k and 50k magnification of Pd-V_2O_5 thin films: (d) un-irradiated; and irradiated with dose (e) 5 kGy; and (f) 250 kGy.

Optical Properties

The UV-vis transmittance spectra measurements were collected in the visible region (400-800nm) of the V_2O_5 and Pd-V_2O_5 thin films to study the characteristic change in the films spectral response upon exposure to different total radiation doses. The changes in transmittance with respect to wavelength of the V_2O_5 and Pd-V_2O_5 films after exposure to gamma irradiation are shown in figure 6a. and 6b. respectively.
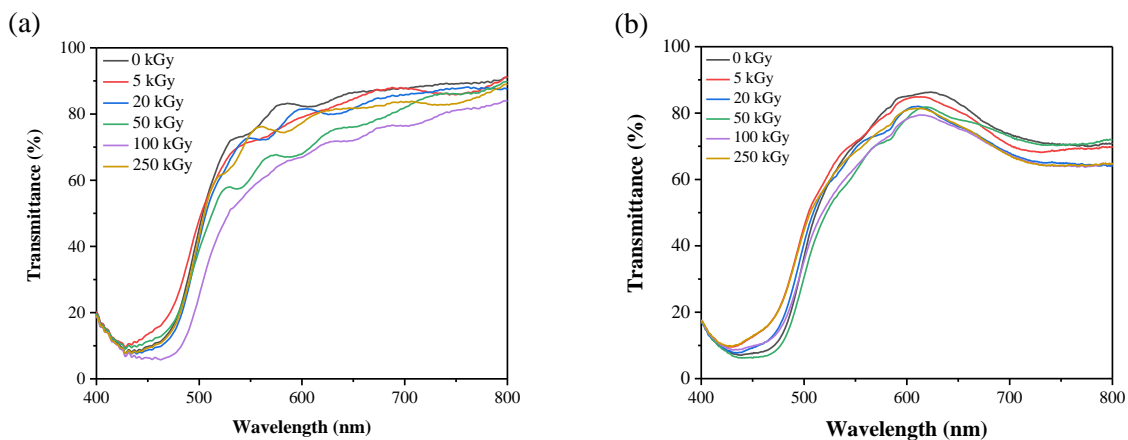

Fig. 6. UV-Vis transmittance spectra obtained following exposure to different total gamma radiation doses for the: (a) V_2O_5 and (b) Pd-V_2O_5 thin films.

UV-Vis spectra are the result of the π-electrons or non-bonding electrons in a molecule absorbing ultra-violet or visible energy to excite these electrons to higher orbitals. Variations in the spectra for the thin films are as a result of changes to the electron structure of the V_2O_5 and $Pd-V_2O_5$ thin films from exposure to gamma radiation. [21] Gamma irradiation may result in the formation of defects in the bandgap of the material and oxygen deficiency (O^-, O^{2-}) in the crystal which provides a competing path for the transition of valence electrons. [1, 22]

The transmittance of the un-irradiated V_2O_5 thin films is generally higher than that of those exposed to gamma irradiation. Overall spectra shape is maintained with a trough at 450 nm and a broad peak above 520 nm. The undulating spectral line suggests that there could be several overlapping transmittance peaks making up the broad peak above 520 nm. The average transmittance of the irradiated V_2O_5 thin films decreases by up to 18% at 600 nm implying that gamma irradiation is altering the V_2O_5 electron structure. [22]

The reflectance of the $Pd-V_2O_5$ thin films varies from that of the V_2O_5 thin films with decreased reflectance above 650nm. This can be attributed to the grey/silver palladium film darkening the sample. However, the effect of gamma irradiation exposure is similar, with decreased transmittance of up to 16% at 600nm. Figure 7 shows the absorption edge shifted to the red region, indicating the reduction of the bandgap of the thin film. This result is consistent with other reports on the gamma irradiation effect on SnO_2 and ZnO samples. [1, 23]
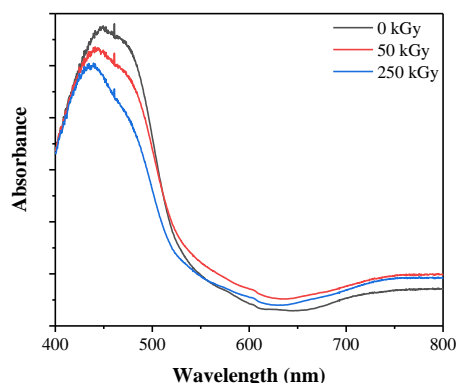

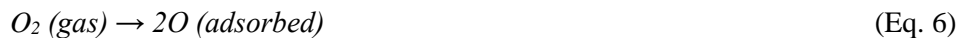Fig. 7. UV-Vis absorbance spectra for the $Pd-V_2O_5$ thin films.

Hydrogen Gas Sensing

The selectivity of vanadium oxide to react with hydrogen can be significantly improved with a thin catalyst film of noble metal such as palladium (Pd). [5] On contact with the catalyst, hydrogen gas is dissociated into hydrogen atoms which diffuse into the interface between the catalyst and metal oxide (V_2O_5). The hydrogen atoms then interact with the V_2O_5 bulk, causing a structural change, resulting in alterations to optical and electrical properties. [23, 24]
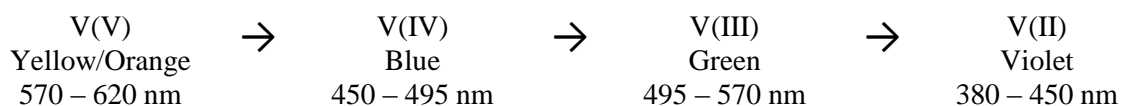
Colour change in the visible region is attributed to the progressive reduction (change in oxidation state) of the metal ions, due to the double injection of electrons and H^+ ions into the V_2O_5 film, forming hydrogen metal bronzes $H_xV_2O_5$ resulting in a chemochromic change. [4] Equation 5 shows a general formula for this reaction. The colour change results from the inter-valence charge transfer of electrons between valence states eg. V^{x+}/V^{x-1+}. [4, 25]

$V_2O_5 + xH^+ + xe^- \leftrightarrow H_xV_2O_5$ (Eq. 5)

The hydrogen atoms are also known to react with chemisorbed oxygen species such as O^{2-} and O^- resulting in the production of water and a free electron as expressed in equations 6-9. [23, 26]

$$O_2 \text{ (gas)} \rightarrow 2O \text{ (adsorbed)} \qquad \text{(Eq. 6)}$$

$$O \text{ (adsorbed)} + e^- \text{ (from } V_2O_5\text{)} \rightarrow O^- \qquad \text{(Eq. 7)}$$

$$H_2 \rightarrow 2H \text{ (adsorbed)} \qquad \text{(Eq. 8)}$$

$$2H \text{ (adsorbed)} + O^- \rightarrow H_2O + e^- \qquad \text{(Eq. 9)}$$

As with many transition metals, vanadium has the ability to adopt multiple oxidation states. Vanadium exhibits four common oxidation states +5, +4, +3 and +2 each of which has a distinguishing colour.

V(V)		V(IV)		V(III)		V(II)
Yellow/Orange	$\rightarrow$	Blue	$\rightarrow$	Green	$\rightarrow$	Violet
570 – 620 nm		450 – 495 nm		495 – 570 nm		380 – 450 nm

In the V_2O_5 thin films, vanadium ions are in the highest oxidation state, 5+, resulting initial orange colour of the Pd-V_2O_5 thin films. [23] Figure 8 shows that upon exposure to 4% H_2 the Pd-V_2O_5 thin films are seen to visually change from orange-brown to a green-black in colour. This colour change is associated with the reduction of the vanadium ion in a +5 oxidation state through the formation of hydrogen vanadium bronzes as shown in equation 5. The visible colour change to green suggests that the vanadium ion adopts an oxidation state of +3 upon reaction with hydrogen.
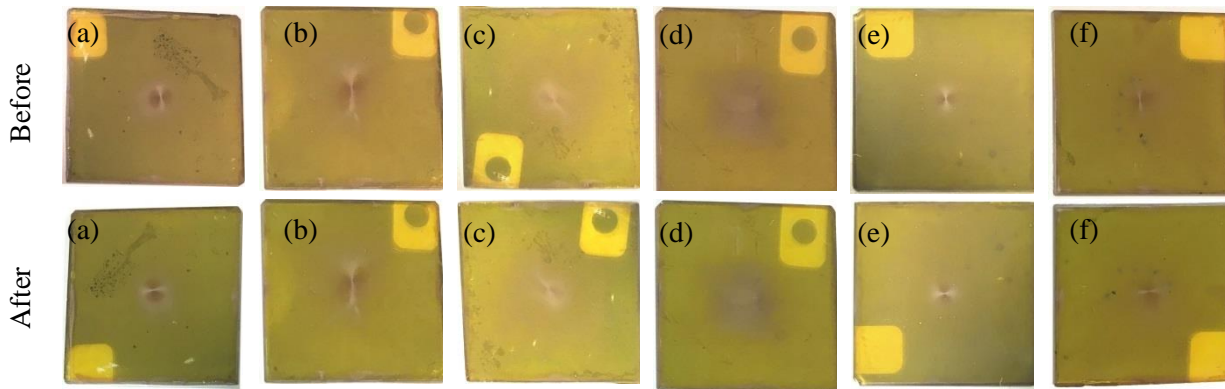

Fig. 8. Images of (a) un-irradiated and the (b) 5 kGy, (c) 20 kGy, (d) 50 kGy, (e) 100 kGy and (f) 250 kGy irradiated Pd-V_2O_5 thin films before and after exposure to 4 % H_2 for 30 minutes.

The UV-Vis spectra of the un-irradiated and irradiated Pd-V_2O_5 films upon exposure to 4% hydrogen were collected to study the effect gamma radiation has on the response to hydrogen. Transmittance spectra were obtained every minute over 30 minutes of exposure to hydrogen. For clarity UV-Vis spectra taken at 10 minute intervals are also plotted for each of the samples in figure 9.
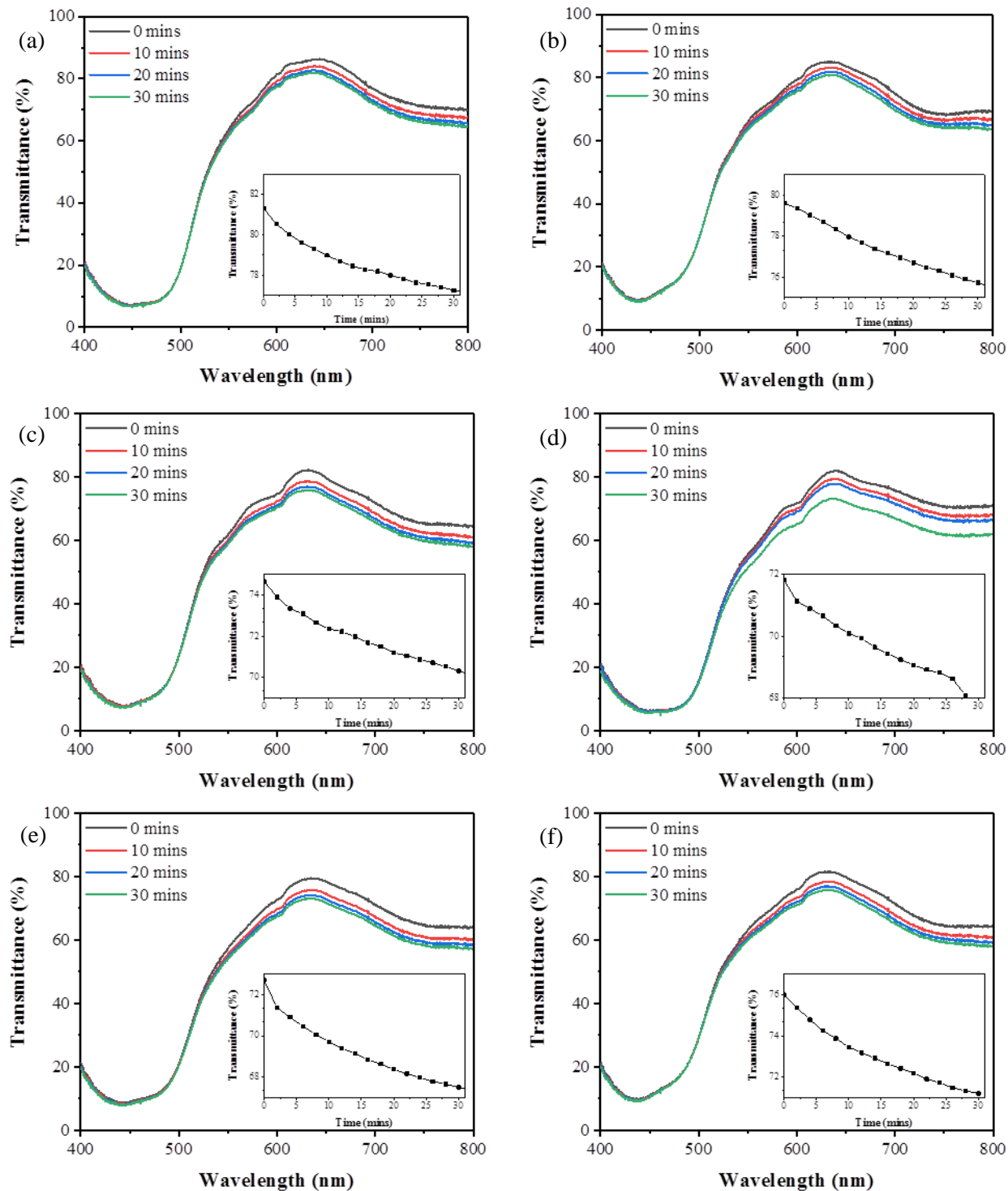
Fig. 9. UV-Vis transmittance spectra of: (a) un-irradiated; and the irradiated Pd- V_2O_5 thin films with irradiation doses of (b) 5 kGy, (c) 20 kGy, (d) 50 kGy, (e) 100 kGy and (f) 250 kGy, exposed to 4% H_2 for 30 minutes. The insets show the dependence of the transmission at 600 nm on time.

When Pd-V_2O_5 thin films are exposed to 4% hydrogen the UV-Vis transmittance is seen to decrease for wavelengths greater than 550nm. This is visually seen by the reduced orange/red colour of the film and darkening of the sample, figure 8. The extent of the decrease in transmittance appears to be independent of the total irradiation dose. The transmittance decreases most significantly during the first 10 minutes exposure to hydrogen suggesting a faster initial rate of reaction with the Pd-V_2O_5 thin films. As the decrease in transmittance slows the Pd-V_2O_5 thin films stop absorbing hydrogen and reach saturation. The insets in figure 9. show the change in transmittance at 600 nm for the Pd-V_2O_5 thin films. In general, the transmittance at 600 nm decreases by 4% during the 30 minutes exposure to hydrogen.

Below a wavelength of 540 nm the transmittance is un-altered during hydrogen exposure. Wavelengths below 540 nm refer to the green-blue section of the visible light spectrum. Vanadium can appear to be green-blue when the ion is in a +4 or +3 oxidation state. The absence of transmittance change below 540 nm suggests that the progressive reduction of the vanadium ions and formation of a hydrogen metal bronze $H_xV_2O_5$, as shown in equation 5, is not occurring. This could be due to the presence of oxygen defects in the V_2O_5 film. The presence of O^{2-} and O^- offers the hydrogen an alternative reaction path, as shown in equation 6-9, reducing the concentration of hydrogen available for the formation of hydrogen vanadium.

No significant variation in the response of the Pd-V_2O_5 thin films to hydrogen is observed at the levels of gamma irradiation investigated. The results suggest that a thin film V_2O_5 sensitised with Pd is a plausible technique for application in the monitoring of hydrogen in low-level radiation environments.

CONCLUSION

In summary, V_2O_5 and Pd-V_2O_5 thin films were synthesised via sol-gel deposition of V_2O_5 followed by electron beam deposition of palladium catalyst. Optical and structural properties of these thin films were studied to clarify the effect of gamma irradiation on the hydrogen sensing characteristics of the Pd-V_2O_5 thin films. At maximum dose (250 kGy) the V_2O_5 thin film begins to show surface degradation; however this is not seen for Pd-V_2O_5 thin films. Generally, the UV-Vis transmittance of the V_2O_5 and Pd-V_2O_5 thin films has decreased with radiation; samples change to a darker brown colour. The rate of colour change on exposure to 4% hydrogen is not effect by increased gamma ray dose from 5 kGy to 250 kGy with a decrease in transmittance of 4% at 600 nm. The results suggest that a thin film V_2O_5 sensitised with Pd is a plausible technique for application in the monitoring of hydrogen in low-level radiation environments.

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