CHARACTERISING THE PERFORMANCE OF HYDROGEN SENSITIVE COATINGS FOR NUCLEAR SAFETY APPLICATIONS

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Abstract

The detection of hydrogen gas is essential in ensuring the safety of nuclear plants. However, events at Fukushima Daiichi NPP highlighted the vulnerability of conventional detection systems to extreme events, where power may be lost. Herein, chemochromic hydrogen sensors have been fabricated using transition metal oxide thin films, sensitised with a palladium catalyst, to provide passive hydrogen detection systems that would be resilient to any plant power failures. To assess their viability for nuclear safety applications, these sensors have been gamma-irradiated to four total doses (0, 5, 20, 50 kGy) using a Co-60 gamma radioisotope. Optical properties of both un-irradiated and irradiated samples were investigated to compare the effect of increased radiation dose on the sensors resultant colour change. The results suggest that gamma irradiation, at the levels examined (>5 kGy), has a significant effect on the initial colour of the thin films and has a negative effect on the hydrogen sensing abilities.

1.0 Introduction

Following the Tohuku 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 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).

Hydrogen management systems on nuclear plants are typically designed to maintain the hydrogen concentration below 1 % hydrogen, significantly below the lower flammability limit (LFL) of 4 %, by systems such as venting. However, in extreme circumstances, such as seen at Fukushima whereby the earthquake and tsunami were more powerful than the plant was designed to accommodate, primary hydrogen management and detection systems may fail leaving the facility vulnerable to hydrogen build up and consequent risk of explosion.

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, relative large, time consuming 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. 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. This phenomenon can be exploited for the detection of hydrogen. [2] Metal oxides such as vanadium oxide (V_2O_5), molybdenum oxide (MoO_3), titanium oxide (TiO_2) 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. [4,5]
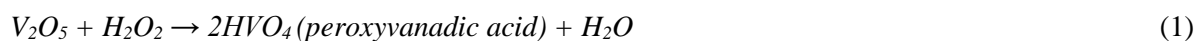
The majority of the developed chemochromic hydrogen sensors have been designed to operate in non-radioactive conditions. In order to use such sensors on nuclear plant, there is therefore a need to characterise the effect of radiation exposure upon their behaviour. Van Duy et al. studied the effect of 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. [1] 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. Shen et al. 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. [6] Similarly, as investigated by Vasanth-Raj et al. it is thought that gamma irradiation would modify the optical properties of TiO_2 by reducing the Ti^{4+} resulting in trapped Ti^{3+} in the solid. [8] This would result in a colour change from transparent to deep blue (~540nm). However, Bello-Lamo et al. show that the radiation above 30 kGy has no effect on the inner crystal structure and the small changes on the surface layer only result in a relatively low (<5 %) reduction is transmittance. [7]

The correlation between gamma irradiation and the hydrogen gas-sensing abilities of metal oxide thin film sensors is important in monitoring hydrogen in nuclear containments with the presence of radioactive sources. There is currently no detailed study in literature about the effect of gamma irradiation on the hydrogen sensing behaviour of vanadium oxide thin films prepared by the sol-gel process. 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 of different total doses, ranging from 5 kGy up to 50 kGy. Sensing performance was measured post irradiation via UV-Vis spectrophotometer.

2.0 Experimental

2.1 Preparation of V_2O_5 coatings

Vanadium pentoxide, V_2O_5, thin films were deposited on indium tin oxide (ITO) 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. [5,7,8] The reaction mechanisms are as follows according to Ren et al. [9]:

$$V_2O_5 + H_2O_2 \rightarrow 2HVO_4 \text{ (peroxyvanadic acid)} + H_2O \tag{1}$$

$$HVO_4 + (n-1)H_2O \rightarrow V_2O_5 \cdot nH_2O + O_2 \tag{2}$$

Prior to deposition, ITO 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. [7]

2.2 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 ~ 4.5×10^{-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.

2.3 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. [10] Pd-V_2O_5 thin films were exposed to gamma irradiation from a Co-60 source at an absorbed dose rate of 200 Gy/min (12 kGy/hour) at room temperature in air atmosphere. To obtain 3 different total irradiation doses of 5, 20, 50 kGy, the irradiation time was varied from 25 to 245 minutes. After gamma irradiation the samples were stored at room temperature in a desiccator until the gas-sensing measurements were performed.

Figure 1. ^{60}Co gamma irradiator

2.4 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 diffuse optical reflectance of the thin films was then measured at room temperature using an Ocean Optics Flame-S-UV-NIR spectrometer at an angle of 45°.
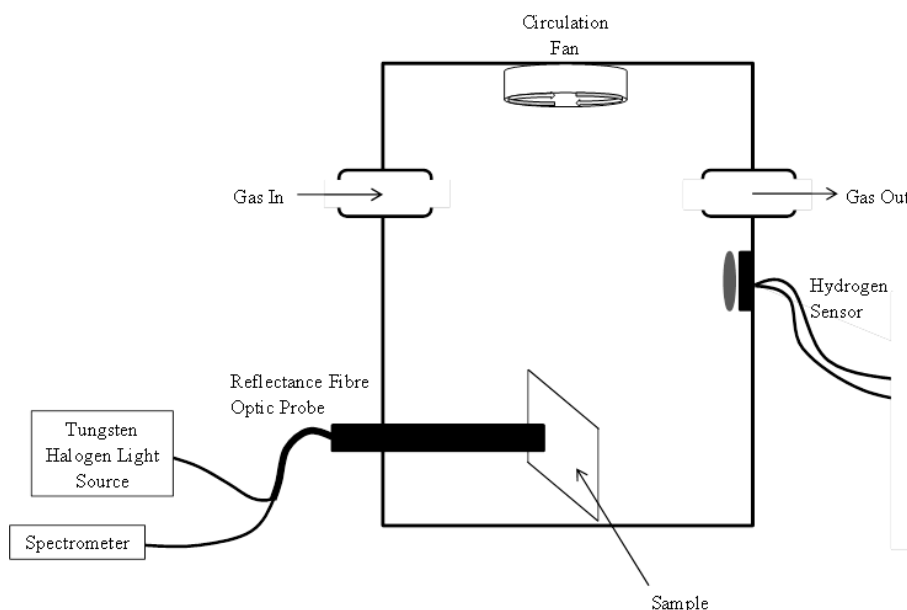
Figure 2. Schematic of hydrogen gas chamber.

3.0 Results and Discussion

3.1 Initial Effect of Gamma Irradiation

The as manufactured Pd- V_2O_5 films are semi-transparent in air. Samples were then irradiated with a Co-60 gamma source at an absorbed dose rate 12 kGy/hour to three different total doses of 5, 20, 50 kGy at room temperature. Visually the samples are seen to darken and the colour appear 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.
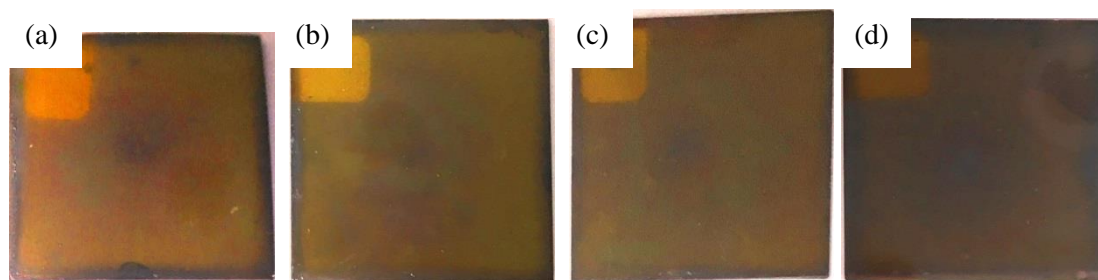

Figure 3. Images of (a) un-irradiated and the (b) 5 kGy, (c) 20 kGy and (d) 50 kGy irradiated Pd-V_2O_5 thin films.

The UV-Vis spectra of the samples were obtained to study the characteristic change in the Pd-V_2O_5 films upon exposure to different gamma doses. Diffuse reflectance spectra measurements were collected in the visible region for un-irradiated and irradiated films. The changes in reflectance with respect to wavelength of the Pd-V_2O_5 films after exposure to gamma irradiation are shown in figure 4.

UV-Vis spectroscopy of crystalline solid V_2O_5 is based on the absorption of suitable energy from incident UV (200-400nm) and visible (400-700nm) light leading to the optical excitation of electron from the valence band to a higher excited energy state. The fraction of light that can be absorbed is specific for materials and varies with chemical and electronic structure. Gamma irradiation may result in the formation of induced defect-centres and oxygen deficiency (O^-, O^{2-}) in the crystal lattice of the

material. Defects in the crystal lattice of Pd-V_2O_5 films cause alterations to the optical band structure of a solid which in turn will alter the UV-Vis spectra obtained. [1,11,12]
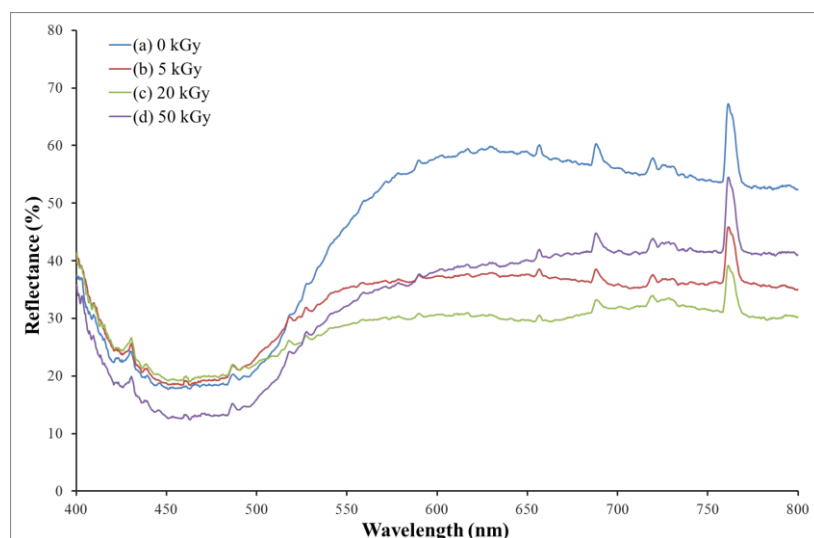

Figure 4. UV-Vis diffuse reflectance spectra of the (a) un-irradiated and the irradiated Pd-V_2O_5 thin films with irradiation doses of (b) 5, (c) 20 and (d) 50 kGy, respectively.

The reflectance of the un-irradiated samples is generally significantly higher than that of the samples exposed to gamma irradiation. The average reflectance of the irradiated thin films decreases by up to 20 % but overall spectra shape is maintained with a trough at 460 nm and broad reflectance peak above 550 nm. Up to 20 kGy total irradiation dose little effect is seen on the reflectance below 520 nm. However, when the thin film is exposed to a higher gamma radiation dose of 50 kGy a significant reduction in reflectance is observed. Above 600 nm the reflectance intensity is significantly reduced with exposure to gamma radiation. However the total radiation dose (of 5 kGy or more) does not initially appear to effect the extent of change in reflectance intensity. The amount of defects may have reached saturation at a lower total dose which explains the similar reflectance intensities for all the irradiated samples. [12]

3.2 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). [4] 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. [13,14]

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. [15] Equation 3 shows a general formula for this reaction. The colour change results from the intervalence charge transfer of electrons between valence states eg. V^{x+}/V^{x-1+}. [15,16]

$$V_2O_5 + xH^+ + xe^- \leftrightarrow H_xV_2O_5 \qquad (3)$$

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 4-7. [13]

$$O_2\ (gas) \rightarrow 2O\ (adsorbed) \qquad (4)$$

$$O\ (adsorbed) + e^-\ (from\ V_2O_5) \rightarrow O^- \qquad (5)$$

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$H_2 \rightarrow 2H \; (adsorbed)$ (6)

$2H \; (adsorbed) + O^- \rightarrow H_2O + e^-$ (7)

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 (Table 1). 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. [13] Figure 5 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 1. The visible colour change to green suggests that the vanadium ions adopt an oxidation state of +3 upon reaction with hydrogen.

Table 1. Colour characteristics of vanadium oxidation states.

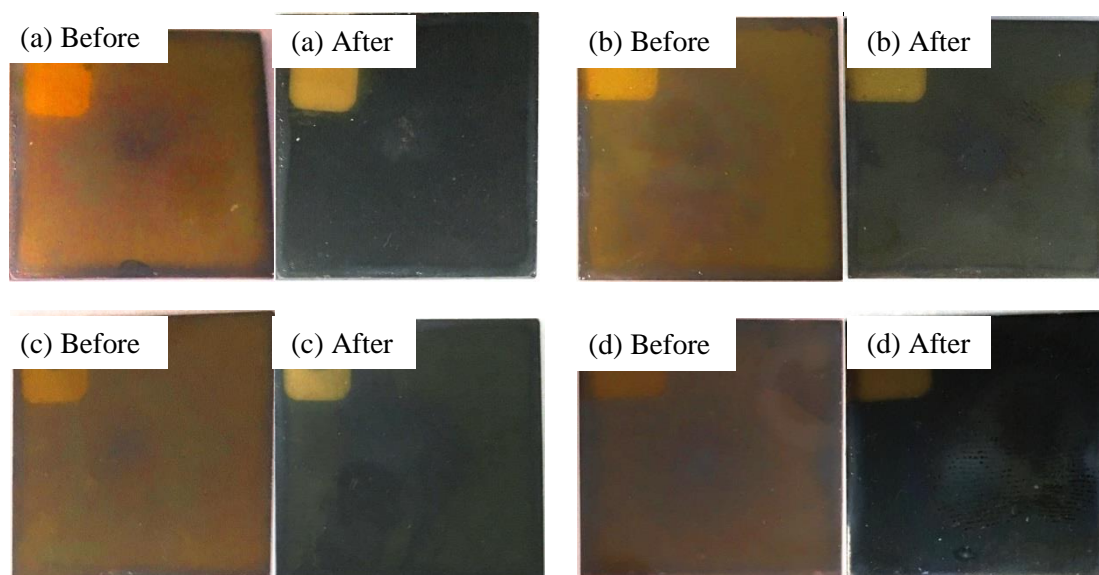| Oxidation state	Colour	Wavelength (nm)
+5	yellow/orange	570 – 620
+4	blue	450 – 495
+3	green	495 – 570
+2	violet	380 – 450

Figure 5. Images of (a) un-irradiated and the (b) 5 kGy, (c) 20 kGy and (d) 50 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 % H_2 were collected to study the effect gamma radiation has on the response to hydrogen. Reflectance spectra were obtained every 2 minutes over 30 minutes of exposure to hydrogen. For clarity UV-Vis spectra taken at 10 minute intervals are plotted for each of the samples in Figure 6.
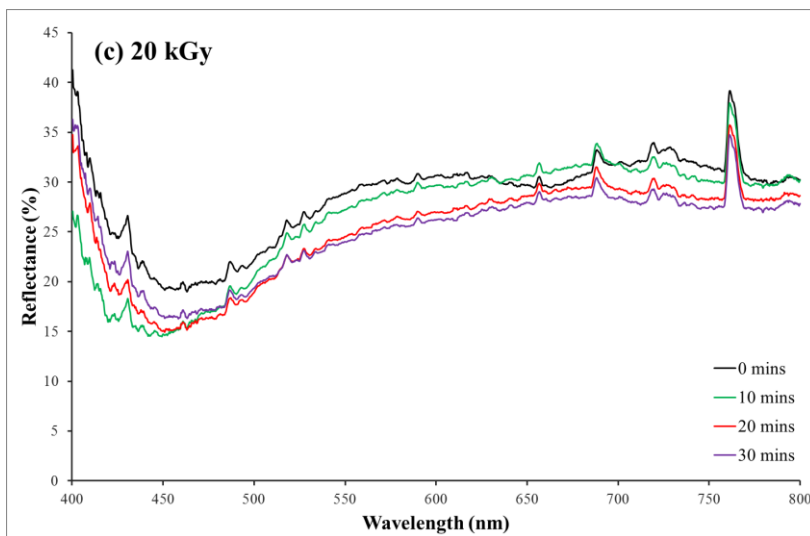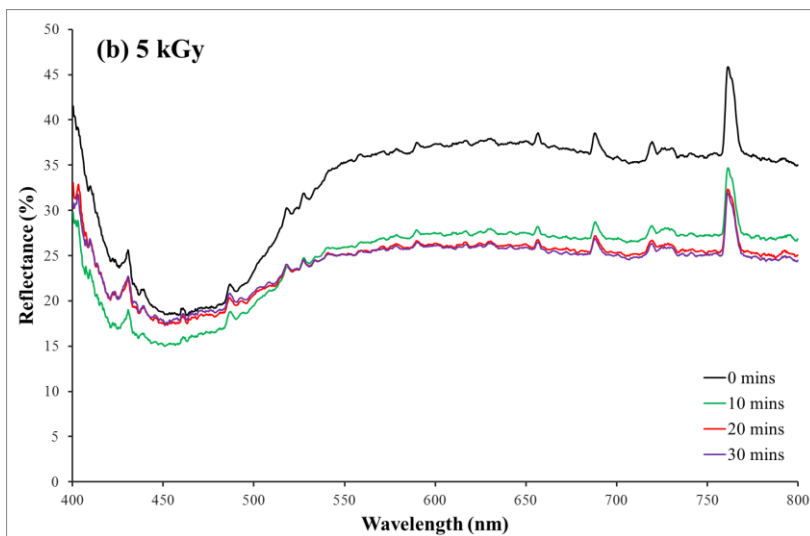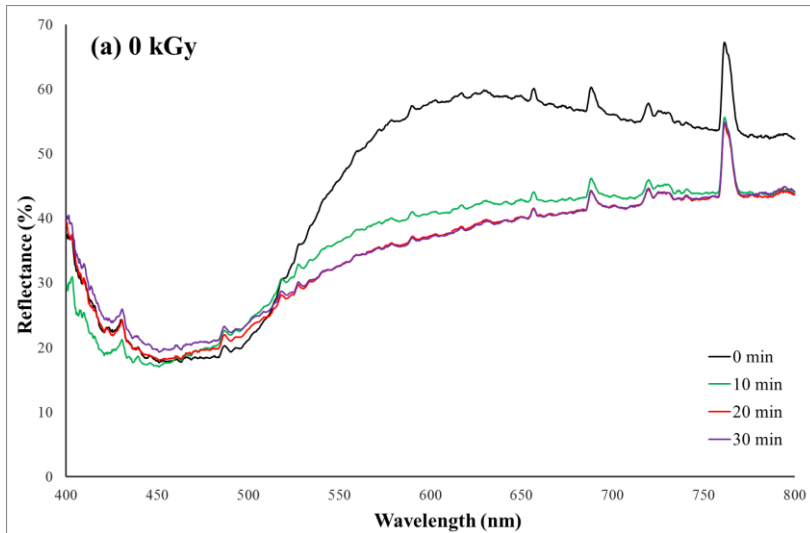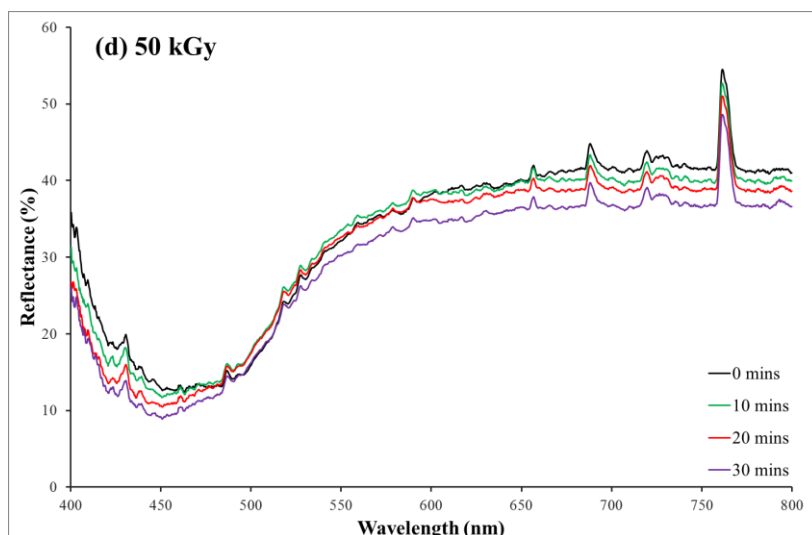
Figure 6. UV-Vis reflectance spectra of (a) un-irradiated and the irradiated Pd-V$_2$O$_5$ thin films with irradiation doses of (b) 5 kGy, (c) 20 kGy and (d) 50 kGy, exposed to 4 % H$_2$ for 30 minutes.

In Figure 6, the UV-Vis reflectance intensity of all the irradiated films is seen to behave in almost the same manner with a decrease in intensity when Pd-V$_2$O$_5$ thin films are exposed to 4 % H$_2$. However, the extent of the decrease in reflectance appears to be dependent on the total irradiation dose. Figure 7 shows the change in reflectance intensity at 750 nm for the un-irradiated and irradiated samples. For the un-irradiated sample and the sample exposed to 5 kGy gamma irradiation the reflectance at 750 nm decreases by around 10 % during 30 minutes exposure to 4 % hydrogen. Additionally, the reflectance intensity does not change after 20 minutes exposure to hydrogen suggesting saturation of the Pd-V$_2$O$_5$ film has occurred. Within the same exposure time the samples irradiated for a total dose of 20 and 50 kGy are seen to have a intensity decrease of just 5 % and appears to still be decreasing after 30 minutes exposure to hydrogen. This suggests that the reaction with hydrogen resulting in the formation of hydrogen vanadium bronzes and the subsequent colour change is slower for Pd-V$_2$O$_5$ thin films exposed to a higher gamma radiation dose. This reduced reaction rate could be due to the increased defects from the higher gamma radiation dose competing for hydrogen. With a greater number of O^{2-} and O$^-$ available for hydrogen to react with, as shown in equations 4-7 a reduced concentration of hydrogen is available for the formation of hydrogen vanadium bronzes.

In the UV-Vis spectra of the un-irradiated and irradiated Pd-V$_2$O$_5$ thin films, Figure 6, below a wavelength of 520 nm the change to reflectance intensity during hydrogen exposure over time does not appear to decrease in the same manner as above 520 nm. Wavelengths below 520 nm refer to the blue/violet section of the visible light spectrum. Vanadium can appear to be blue/violet when the ion is in a +4 oxidation state which corresponds to the formation of HV$_2$O$_5$ hydrogen vanadium bronze. For samples exposed to 0, 5 and 20 kGy the reflectance intensity initially decreases over the first 10 minutes of hydrogen exposure before gradually increasing again over longer exposure times. However, for 50 kGy a gradual decrease in reflectance intensity with exposure time is seen. This would suggest that the rate of reduction with hydrogen (Equation 3) has decreased with increased radiation exposure slowing the formation of HV$_2$O$_5$ and subsequent reduction to H$_2$V$_2$O$_5$.

To fully understand the effect that gamma irradiation has on the bulk V$_2$O$_5$ chemochromic film, further investigation is now required including surface analysis, increased hydrogen exposure times and increased gammas irradiation doses.
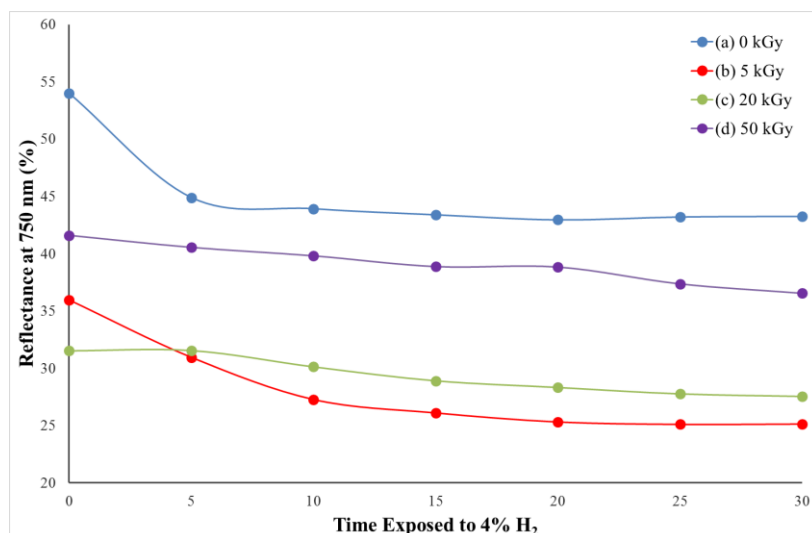
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Figure 7. Comparison of reflectance intensity at 750 nm for (a) un-irradiated and the irradiated Pd-V_2O_5 thin films with irradiation doses of (b) 5 kGy, (c) 20 kGy and (d) 50 kGy, exposed to 4% H_2 for 30 minutes.

4.0 Conclusion

In summary, Pd-V_2O_5 thin film sensors were synthesised via sol-gel deposition of V_2O_5 followed by electron beam deposition of palladium catalyst. Optical properties of these thin films were then studied via UV-Vis diffuse reflectance spectrometery to clarify the effect of gamma ray irradiation on the hydrogen gas sensing characteristics of the Pd-V_2O_5 thin films. Generally, the reflectance of Pd-V_2O_5 films have changed significantly with irradiation: samples change to a darker green-brown colour depending on gamma radiation dose. The rate of colour change on exposure to 4 % hydrogen decreases as the gamma ray dose is increased from 5 kGy to 50 kGy. The results suggest that gamma irradiation generates defects in the bulk structure of V_2O_5 altering the gas-sensing abilities of the films.

5.0 Acknowledgement

6.0 References

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