



## Effects of oxygen partial pressure on structural and gasochromic properties of sputtered VOx thin films

Wei-Luen Jang<sup>a</sup>, Yang-Ming Lu<sup>b</sup>, Ying-Rui Lu<sup>a,c</sup>, Chi-Liang Chen<sup>d</sup>, Chung-Li Dong<sup>a,\*</sup>, Wu-Ching Chou<sup>e</sup>, Jeng-Lung Chen<sup>a</sup>, Ting-Shan Chan<sup>a</sup>, Jyh-Fu Lee<sup>a</sup>, Chih-Wen Pao<sup>a</sup>, Weng-Sing Hwang<sup>f</sup>

<sup>a</sup> National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

<sup>b</sup> Department of Electrical Engineering, National University of Tainan, Tainan 70005, Taiwan

<sup>c</sup> Program for Science and Technology of Accelerator Light Source, National Chiao Tung University, Hsinchu 30010, Taiwan

<sup>d</sup> Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

<sup>e</sup> Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

<sup>f</sup> Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

### ARTICLE INFO

Available online 5 March 2013

#### Keywords:

VOx film  
Gasochromic  
H<sub>2</sub> sensor

### ABSTRACT

VOx films were deposited by radio-frequency reactive magnetron sputtering from a vanadium target in an Ar–O<sub>2</sub> gas mixture and pure O<sub>2</sub>. For the films deposited in the gas mixture, the Ar flow rate was controlled at 20 sccm and the oxygen flow rate was controlled at 1, 3, and 5 sccm, respectively. A thin (~5 nm) Pt layer was deposited on the VOx thin films as a hydrogen catalyst. The long-range structural order, short-range atom arrangement, and gasochromic properties of the deposited films were studied. The grazing incidence X-ray diffraction (GIXRD) results indicate that the deposited films are amorphous. Lamellar structures were found at oxygen flow rates of 3 sccm and above. The X-ray absorption spectroscopy (XAS) results show that the short-range atom arrangement of the lamellar VOx thin films is similar to that of crystal V<sub>2</sub>O<sub>5</sub>. The GIXRD and XAS results show that the film obtained with the gas mixture and at an oxygen flow rate of 1 sccm did not significantly change after exposure to hydrogen, whereas the other films exhibited decreased interlayer distance, oxidation state, and crystallinity. The color of the films changed from light or deep yellow to gray. The results suggest that the gasochromic properties of the VOx thin films are related to the V<sub>2</sub>O<sub>5</sub>-like atom arrangement and the interlayer distance of the lamellar structure. The films deposited with an oxygen flow rate of 3 sccm and above can be applied to H<sub>2</sub> gas sensors.

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### 1. Introduction

Hydrogen is considered as a candidate alternative energy source. However, hydrogen tends to explode in air when its concentration is above 4% [1]. The development of hydrogen sensors is thus important for hydrogen energy applications. Hydrogen sensors based on the gasochromic properties of metal oxide thin films have been proposed [1–5]. The films change color and oxidation state when exposed to hydrogen. This type of sensor is safer than that based on the measurement of electrical conductivity since the sensor does not introduce any additional ignition source.

V<sub>2</sub>O<sub>5</sub> thin films have been studied for application in H<sub>2</sub> sensors [1–5]. A thin layer of palladium (Pd) or platinum (Pt) is deposited on the film surface to act as a catalyst to dissociate hydrogen molecules. The hydrogen atoms diffuse into the V<sub>2</sub>O<sub>5</sub> layer and cause a change in the optical transmittance. Although the related phenomena have been reported, the change in the electronic structure and atomic

structure during the coloration are not fully understood yet. In addition, the long-range structural order and the short-range atom arrangement of amorphous vanadium oxides prepared by sputtering deposition have not been reported to date. In this study, VOx thin films are prepared by radio-frequency (RF) reactive magnetron sputtering. The effects of oxygen partial pressure on film structure, oxidation state, and gasochromic properties are studied.

### 2. Experimental methods

VOx films were deposited on a Corning 1737 substrate using an RF reactive magnetron sputtering system with a vanadium (V) target. The working power was fixed at 150 W and the sputtering deposition was performed at a gas pressure of 1.33 Pa in pure O<sub>2</sub> (sample s0) and an Ar–O<sub>2</sub> gas mixture. For the Ar–O<sub>2</sub> gas mixture, the Ar flow rate was controlled at 20 sccm and the oxygen flow rate was controlled at 1 (s1), 3 (s3), and 5 (s5) sccm, respectively. The film thickness of the deposited films was controlled at 200 nm. The sputtering time for s1, s3, s5, and s0 were 15, 40, 62, and 125 min, respectively. A thin (~5 nm) Pt layer was deposited on the VOx thin films as a

\* Corresponding author. Tel.: +886 3 5780281x7106; fax: +886 3 5789816.  
E-mail address: [dong.cl@nsrrc.org.tw](mailto:dong.cl@nsrrc.org.tw) (C.-L. Dong).

hydrogen catalyst. In the gasochromic reaction, the films were exposed to hydrogen at 1 atm and 25 °C for 2 h. The crystal structure of the deposited film was measured by grazing incidence X-ray diffraction (GIXRD). The oxidation state and the surroundings of the vanadium atoms were measured by X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. The absolute energy positions were calibrated by V (5465 eV) metal foil. The V K-edge spectra were collected in the fluorescence mode and the angle between the X-ray beam and the films was 45°. The XAS measurements were conducted at wiggler beamline BL17C at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan.

### 3. Results and discussion

Fig. 1 shows the GIXRD patterns of the as-deposited VOx thin films before (black lines) and after gasochromic reaction (red lines). No diffraction peaks appear in s1, whereas one broad peak at ~6° appears in the other films. The broad peak slightly shifts to lower angles with increasing oxygen flow rate during deposition. After gasochromic reaction, the peak position shifts to a higher angle, and the peak intensity markedly decreases. The GIXRD patterns change most for the film deposited in pure O<sub>2</sub>. The GIXRD patterns of s1 remain unchanged after gasochromic reaction. The insets show photographs of the films before and after gasochromic reaction. s1 is initially black, and almost unchanged after gasochromic reaction. s3 and s5 are initially light yellow, becoming gray after gasochromic reaction. sO changes from deep yellow to dark gray after gasochromic reaction.

The GIXRD results indicate that the structure of the deposited films is amorphous and that the broad peak for s3, s5, and sO is related to the (001) peak of lamellar materials [6]. According to the reported literature [6], the XRD pattern of V<sub>2</sub>O<sub>5</sub>·1.6H<sub>2</sub>O xerogel shows (001), (003), (004), and (005) peaks. The (00l) peaks indicate that the film is composed of ribbon-like species and has lamellar ordering. Also, it is considered as an intercalation compound, in which there is a reversible intercalation of mobile guest species (atoms, molecules, or ions) into a crystalline host lattice. V<sub>2</sub>O<sub>5</sub>·1.6H<sub>2</sub>O disappears and V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O forms when the film is heated. After this transformation, the (003), (004), and (005) peaks almost disappear and the intensity of (001) dramatically decreases. The diffraction pattern of V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O also suggests a lamellar structure, in which the interlayer distance is shorter than that of V<sub>2</sub>O<sub>5</sub>·1.6H<sub>2</sub>O ( $d_{V_2O_5 \cdot 1.6H_2O} = 11.57 \text{ \AA}$ ;  $d_{V_2O_5 \cdot 0.5H_2O} = 8.75 \text{ \AA}$ ). In this study, only the (001) peak was

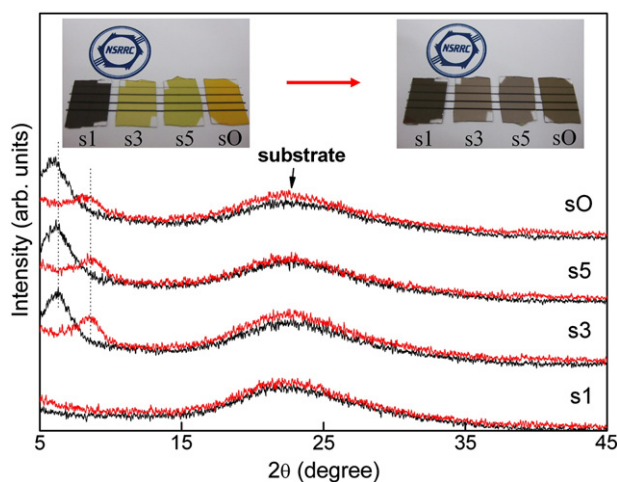


Fig. 1. GIXRD patterns of as-deposited VOx thin films before (black lines) and after (red lines) gasochromic reaction. The insets show photographs of the films before (left) and after (right) gasochromic reaction.

found. The interlayer distances of s3, s5, and sO obtained from the Bragg's law are 14.2, 14.4, and 14.7 Å, respectively. The results indicate that the sputtered films exhibit a lamellar structure. The initial color of the as-deposited films is determined by the oxygen content in the films which is controlled by the introduced oxygen flow rate during deposition. After gasochromic reaction, the changes in the GIXRD patterns indicate that the interdiffusion of hydrogen atoms reduces the interlayer distance and disorders the lamellar structure. According to the GIXRD patterns and photographs, s3, s5, and sO can be applied to H<sub>2</sub> gas sensors. Also, a greater interlayer distance benefits the gasochromic reaction.

It is known that GIXRD provides an average structure of the crystalline phase with a long-range structural order, whereas XAS is atom-specific and capable of probing the short-range structure around the targeted atom. Due to the amorphous nature of the films, their structural information and oxidation state cannot be obtained from Fig. 1. Fig. 2 shows the V K-edge spectra of the deposited VOx thin films and the standards (VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>). Insets (a) and (b) respectively show the pre-edge region and the main absorption edge area of the deposited films and the standards. The VO<sub>2</sub> standard was obtained via the two-stage thermal annealing of sO. sO was first annealed at 360 °C in a 90% Ar–10% H<sub>2</sub> mixture for 3 h. The film was then annealed at 500 °C in pure N<sub>2</sub> for 1 h. The V<sub>2</sub>O<sub>5</sub> standard was obtained by annealing sO at 500 °C in air for 2 h. The crystalline structures of the standards were confirmed by GIXRD. The results are shown in Fig. 3. The V K-edge features of the standards are consistent with those reported in the literature [7,8].

In Fig. 2, pre-edge peak A is due to the formally forbidden 1s → 3d electronic transition, which is dipole-allowed if the full local octahedral symmetry is decreased [7,8]. The crystal structure of VO<sub>2</sub> is monoclinic, which can be regarded as a distorted rutile structure [8]. The vanadium atoms are six fold-coordinated by oxygens and are displaced from the center of the octahedron. In the V<sub>2</sub>O<sub>5</sub> crystalline, the vanadium atoms are placed in skew pyramidal oxygen coordination with one additional

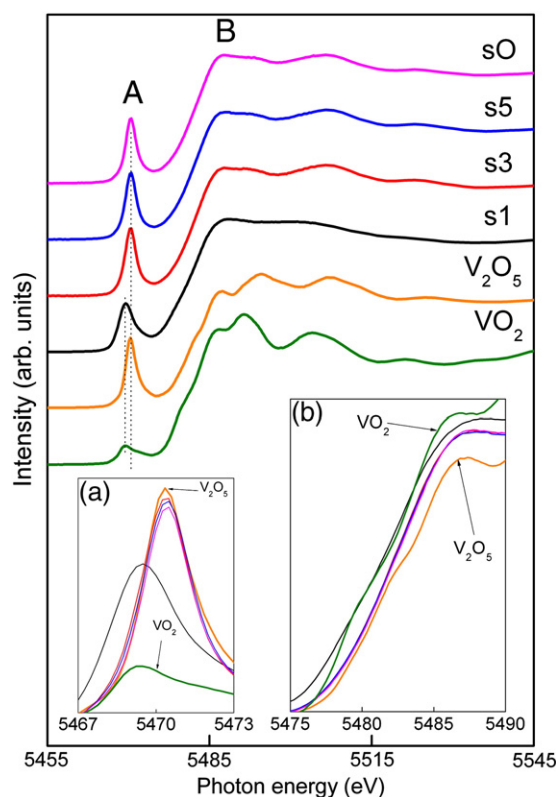


Fig. 2. V K-edge spectra of as-deposited VOx thin films and standards (VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>). The insets show (a) pre-edge region and (b) main absorption edge area of the films.

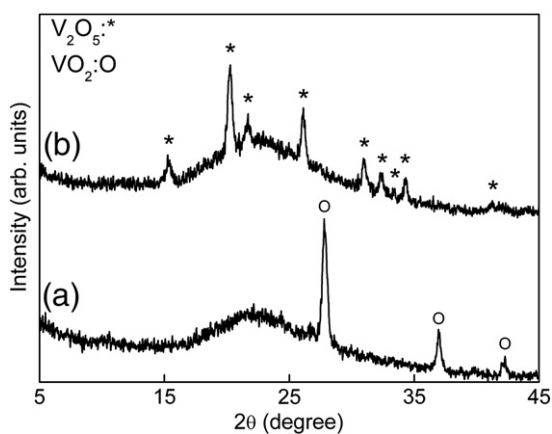


Fig. 3. GIXRD patterns of (a)  $\text{VO}_2$  and (b)  $\text{V}_2\text{O}_5$ .

axial oxygen atom at a much further distance [7]. The geometry leads to a higher distorted octahedral coordination sphere for the vanadium atoms. The pre-edge peak intensity is affected by the vertical symmetry of apical V–O bonds in  $\text{V}_2\text{O}_5$  films [9]. Peak B corresponds to the resonances of the photoelectrons which is due to transitions from core levels to non-binding levels in the continuum. The peak is greatly affected by the symmetry of the four basal oxygens surrounding the vanadium sites [9,10].

The oxidation state of vanadium can be determined from the XANES spectrum, including the energy of pre-edge peak and the main absorption edge [8]. As shown in inset (a) in Fig. 2, the energy position of the pre-edge peak of s1 is close to that of the  $\text{VO}_2$  standard and those of the others are close to that of the  $\text{V}_2\text{O}_5$  standard. Likewise, the main absorption edge (inset (b)) of s1 almost overlaps that of the  $\text{VO}_2$  standard and those of the other films are shifted to high photon energies close to the  $\text{V}_2\text{O}_5$  standard. The oxidation states of the  $\text{VO}_2$  and  $\text{V}_2\text{O}_5$  are +4, and +5, respectively. Consequently, both results indicate that the oxidation state of s1 can be determined as +4, and those of the others are slightly lower than +5.

Further observation of inset (a) indicates that the pre-edge intensities of s3, s5, sO, and  $\text{V}_2\text{O}_5$  standard are comparable and the overall absorption spectrum appear like that of amorphous  $\text{V}_2\text{O}_5$  prepared by rapid quenching [10] and the sol–gel method [9]. Moreover, the local atomic structure of amorphous  $\text{V}_2\text{O}_5$  has a great resemblance to that of crystal  $\text{V}_2\text{O}_5$  [9,10]. As a result, the short-range atom arrangements of s3, s5, and sO are close to that of crystal  $\text{V}_2\text{O}_5$ . The difference in pre-edge peak intensity and features of edge resonance between the deposited films (s3, s5, and sO) and crystal  $\text{V}_2\text{O}_5$  are related to the less split apart of V–O apical bonds [9] and the less distorted arrangement of the four basal oxygens [10].

EXAFS is a final state interference effect involving the scattering of outgoing photoelectrons from neighboring atoms. The structure parameters can be obtained by converting the photon energy into photoelectron wavevector  $\kappa$  [11]. The  $\kappa^3$ -weighted EXAFS were studied to further investigate the short-range atom arrangements of the films. Fig. 4 shows the  $\kappa^3$ -weighted EXAFS at the V K-edge of the films. The figure clearly shows that the EXAFS oscillation of s1 is far from those of the other films and the standards, whereas those of s3, s5, sO, and the  $\text{V}_2\text{O}_5$  standard are similar. The results confirm the similarity in the short-range atom arrangement of s3, s5, sO, and crystal  $\text{V}_2\text{O}_5$ . The difference found at  $\kappa = 7.5 \text{ \AA}^{-1}$  is due to the modification of the V–O bonds mentioned above and can be used to distinguish amorphous and crystal  $\text{V}_2\text{O}_5$ . This result agrees with the earlier reports [9,10].

Fig. 5 shows the V K-edge spectra of the deposited VOx thin films before and after gasochromic reaction. The inset shows the  $\kappa^3$ -weighted EXAFS curves of sO before and after gasochromic reaction. The spectrum

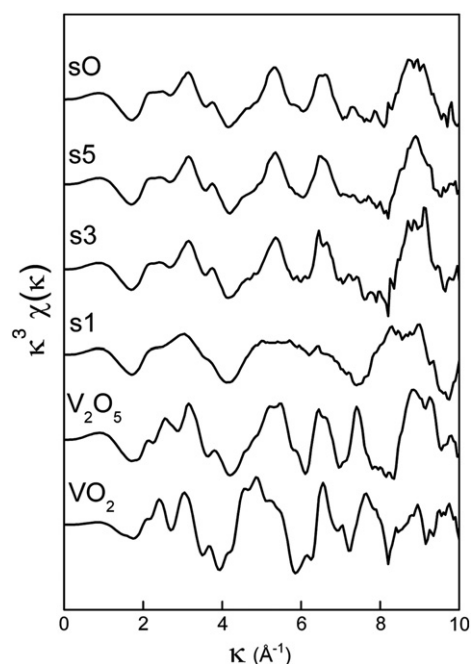


Fig. 4.  $\kappa^3$ -weighted EXAFS curves at the V K-edge of as-deposited films and standards ( $\text{VO}_2$  and  $\text{V}_2\text{O}_5$ ).

is almost unchanged in s1 before and after gasochromic reaction. However, the shift of the main absorption edge to low photon energy accompanies the reduction of pre-edge intensity are observed in s3, s5 and sO after gasochromic reaction. The results indicate that s1 has weaker reaction with hydrogen atoms compared to other which correspond with the poor gasochromic coloration displayed by s1 (inset in

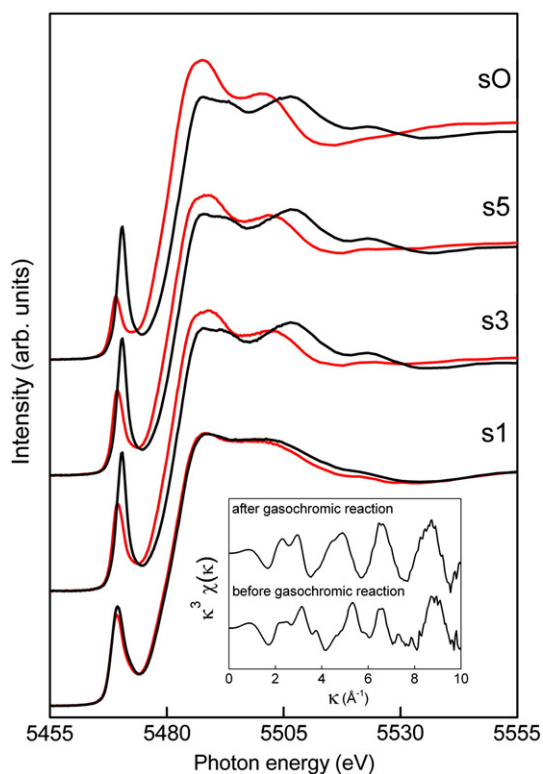


Fig. 5. V K-edge spectra of as-deposited VOx thin films before (black) and after (red) gasochromic reaction. The inset shows the  $\kappa^3$ -weighted EXAFS curves of sO before (black) and after (red) gasochromic reaction.

Fig. 1). The films with a  $V_2O_5$ -like atom arrangement and lamellar structure benefit the gasochromic reaction. The changes in K-edge absorption spectra suggest that the gasochromic reaction is strongly related to a decrease in the oxidation state of vanadium and accompanied by an increase in octahedral symmetry.

As shown in the inset, the EXAFS oscillations of sO are disordered, becoming more coherent in the  $k$  range of 4–10  $\text{\AA}^{-1}$ . It is known that the EXAFS oscillations of a crystal  $V_2O_5$  are composed of many sine waves and each of them corresponding to a V–O bond with the same distance. The coherence of EXAFS oscillations implies an equalization of V–O distance after gasochromic reaction, which is consistent with the results reported for Li intercalated  $V_2O_5$  xerogel [12] and  $Li_xV_2O_5$  bronzes [13]. The gasochromic reaction of VOx films in this study can be pictured as intercalated H atoms reducing the oxidation state of vanadium and the discrepancy in V–O distances. The geometry change then reduces the interlayer distance and disorders the lamellar structure, as shown in Fig. 1.

#### 4. Conclusion

The local atomic structural and gasochromic properties of sputtered VOx thin films were studied by GIXRD and XAS. Films deposited at 150 W on an unheated substrate were amorphous. Lamellar structures were found in films deposited at oxygen flow rates of 3 sccm and above. The XAS results indicate that the short-range atom arrangements of the lamellar VOx films are similar to that of crystal  $V_2O_5$ . The gasochromic reaction of VOx films results from the intercalation of hydrogen atoms reduces the oxidation state of vanadium and the discrepancy in V–O bond distances. The changes in the oxidation state and V–O bond distance are responsible for the coloration and structural change shown in GIXRD, respectively. The gasochromic properties of the VOx thin

films were found to be correlated with the short-range atom arrangement and the interlayer distance of the lamellar structure. The  $V_2O_5$ -like atomic arrangement and a great interlayer distance benefit the gasochromic properties of sputtered VOx.

#### Acknowledgments

This study was financially supported by the National Science Council of Taiwan under grants NSC 98-2112-M-213-006-MY3, 99-2112-M-001-036-MY3, 99-2221-E-024-003, and 97-2221-E-006-006-MY3.

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