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Tunable thermochromic properties of V₂O₅ coatings

Sunil Kumar ^a, Francis Maury ^b, Naoufal Bahlawane ^{a,*}

^a Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette Luxembourg

^b CIRIMAT, ENSIACET, 4 Allée E. Monso, 31030 Toulouse, France

A B S T R A C T

Thermochromic Di vanadium pentaoxide (V₂O₅) coatings displaying a variety of colours were synthesised. Tuning of thermochromic behaviour was achieved via a controlled oxidative annealing under ambient air of the as-grown VO_x films. Adjusting the oxygen deficiency in V₂O₅, allows tuning the colour of the films and as a consequence its thermochromic behaviour. Non oxygen deficient V₂O₅ did not feature any measurable thermochromism

Keywords:

Vanadium pentaoxide

Thermochromic

Tuning

Coatings

Chemical vapor deposition

1. Introduction

Thermochromic materials display a perceptible change in colour upon temperature variations [1–3]. This behaviour is observed in several types of compounds, ranging from organic molecules [4,5], inorganic compounds [6,7], organometallic [8,9], and transition metal oxides [10–12]. Due to the simplistic nature of temperature dependent colour changing ability, they are utilized in several devices like temperature sensor [13–15], information display [16,17], safety devices and food packaging [18,19]. Nevertheless, there has been a considerable interest in obtaining compounds with a control over the colour of the thermochromic materials. In terms of the temperature at which thermochromic transition occurs, as well as the colours they exhibit during transition [20–23]. Hence, tunable thermochromic compounds are expected to widen their scope of applications.

Tuning of thermochromic behaviour can be implemented by several mechanisms. Physical mixing of two or more thermochromic pigments was used to adjust the perceived colour [24,25]. In chemical pathways, the constituents are modified to alter the optical properties and produce the desired colour. In Leuco dyes,

changing the alkyl chain lengths in developer or solvent impacts the thermochromic nature of the dye [26,27]. In transition metal oxides (TMO) tuning of optical properties and thermochromism is achieved by the help of chemical doping [28,29]. Dopants fill the interstices or replace the host atom to modify the band gap by forming additional donor or acceptor levels, which facilitate inter band transitions.

In addition to conventional doping methods, creating oxygen vacancies emerges as an efficient technique to alter the optical properties [30,31]. The obtained optical properties are stable as far as the oxygen vacancy level is maintained. Generating oxygen vacancies is in fact analogous to self-doping. In case of tungsten oxide [32], it has been demonstrated that vacuum annealing leads to loss of oxygen with a consequent impact on the optical properties. Chromium oxide (Cr₂O₃), a widely studied TMO for its chromic properties, shows a variation in optical properties after annealing at adjusted oxygen partial pressures [11]. Although the control of oxygen vacancies in TMO can significantly impact their optical properties, it has not been proposed as an approach to adjust their thermochromic behaviour.

There have been several studies correlating the oxygen vacancies in V₂O₅ to variation in electro-chemical and optical properties. However thermochromic tuning linked to the adjusted sub-stoichiometry has not been reported so far. The present study deals with the tuning of thermochromic properties of V₂O₅ coatings, to achieve fine control over the perceived colour and thermally induced colour change.

* Corresponding author.

E-mail address: naoufal.bahlawane@list.lu (N. Bahlawane).

2. Experimental

2.1. Preparation of V_2O_5 coatings

Thin films of vanadium oxide were deposited on silicon substrates by Direct Liquid Injection (DLI) Metal Organic Chemical Vapor Deposition (MOCVD), the details of which are reported elsewhere [33,34]. Argon was used as the carrier gas at a flow rate of 50 sccm while the chamber pressure was adjusted to 10 mbar. Substrates were maintained at a constant temperature of 500 °C during the 4 h of deposition.

After deposition, samples were allowed to cool till room temperature in argon atmosphere at low pressure before withdrawing from the chamber. Further handling of the samples was carried out under ambient atmosphere. Post deposition annealing was performed under ambient air at 300–580 °C. The annealing time was adjusted to allow a complete oxidation from VO_x to V_2O_5 . While 10 min were sufficient for oxidation at 550 °C, significantly longer times were required at lower temperatures; this can be explained by simple temperature dependent oxidation kinetics.

To isolate V_2O_5 coatings from atmospheric gas phase interactions, Atomic Layer Deposition (ALD) of Al_2O_3 was performed using the sequential introduction of Trimethylaluminium (TMA) and water. The pulse times for each reactant were adjusted to 40 ms with a 15 s purge in between each pulse. The rather large pulse and purge times were chosen to achieve complete conformal coverage over the film. ALD was carried out at 120 °C under partial pressure of 2 mbar and Argon was used as the carrier gas at a flow rate of 50 sccm.

2.2. Film characterization

Total hemispherical reflection (THR) measurements were carried out on LAMBDA 1050 UV/Vis/NIR spectrophotometer from Perkin Elmer with a 150 mm integration sphere in the reflection configuration. Measurements, which correspond to the sum of specular and diffuse reflections, were performed in the visible spectral range (400–800 nm). Temperature-dependent measurements were carried out with the help of a custom made sample holder with an integrated heating element. Temperature control was achieved by a Horst HT 60 temperature controller coupled to a K-type thermocouple.

The film thickness and roughness were measured using an Alpha step d-500 Profilometer from KLA-Tencor and the cross-section inspection with FEI Helios Nanolab 650™ Scanning electron microscopy (SEM). Surface morphology was characterized by SEM at a working distance of 4 mm with an acceleration voltage of 5 kV. X-ray diffraction (XRD) was used to characterize the films using the Bruker D8, with $CuK\alpha$ as the X-ray source. Data were collected in the θ -2 θ (locked couple) mode from 2 θ of 10°–30° with a step size of 0.02°.

3. Results and discussion

The as-deposited VO_x films feature a dark grey colour. A relatively high growth rate of 37.5 nm/min was recorded. VO_x films were oxidised under ambient air at various temperatures ranging from 350 to 580 °C until the films displayed a complete oxidation. This time was adjusted from 60 min at 350 °C to 10 min at 580 °C. Films changed from dark grey to bright orange or crimson red indicating successful oxidation to V_2O_5 .

V_2O_5 films obtained by oxidative annealing at 350°C- 400 °C appear lime green at room temperature. Coatings obtained at oxidation temperature of 450 °C - 475 °C were bright yellow. Whereas, coatings oxidised at 500 °C - 550 °C appeared honey

yellow and coatings oxidised at 580 °C appear metallic grey.

It is worth noting that V_2O_5 colours ranging from green to honey yellow were reported earlier by Aita et al. [35]. The authors associated the colour of sputter deposited V_2O_5 films with different oxygen partial pressures. It was observed that films deposited with low O_2 partial pressures appeared green, whereas films with higher O_2 partial pressure were yellow. The change of colour from green to honey yellow is attributed to a decreased oxygen deficiency and is in line with our observation.

X ray diffraction patterns of films oxidised at various temperatures, shown in Fig. 1(a), indicate the formation of pure phase polycrystalline V_2O_5 throughout the range of oxidation temperature. The peaks at $2\theta = 15.3, 20.3, 21.8$ and 26.1 are assigned to the (200), (001), (101) and (110) lattice planes of orthorhombic structure of V_2O_5 (PDF- 000411426). Higher oxidation temperatures (500 °C) improved the crystallinity and resulted in strongly 'c'-oriented films. This is attributed to the increased coalescence to form larger crystallites as shown in Fig. 1(b). No measurable variation in the lattice parameters could be observed.

Films feature a highly porous morphology at the oxidation temperatures of 350 °C and gradually transform to large crystallites at 550 °C with reduced porosity. The average crystallite size, calculated using the Scherrer's equation increased from 130 nm for films oxidised at 350 °C to about 800 nm for films that have undergone oxidation at 550 °C. Alongside the increase in crystallite size, the surface roughness of the coatings increased linearly with oxidation temperature as shown in Fig. 1 of ref [36].

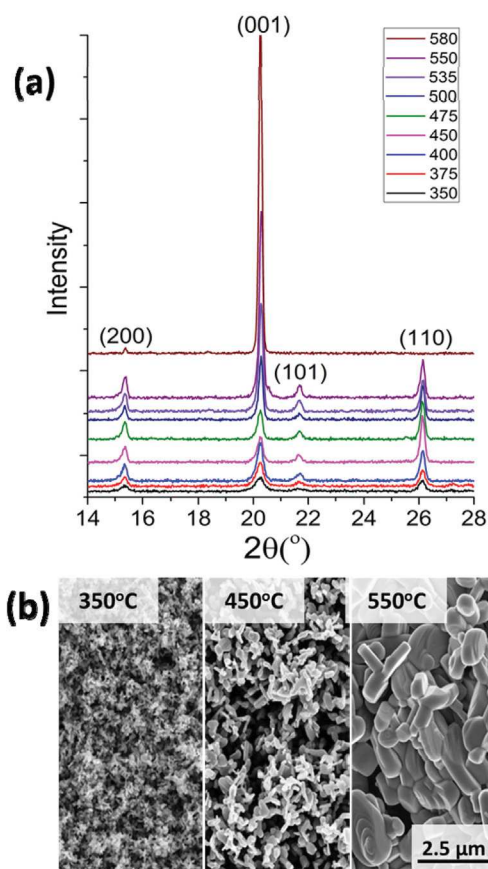


Fig. 1. (a) X-Ray diffractograms of V_2O_5 films oxidised at different temperatures reveal formation of pure, single phase orthorhombic structure as per PDF no [000411426] and (b) surface scanning electron micrographs of the oxidised films at 350 °C, 450 °C and 550 °C.

In order to distinguish the optical properties of V_2O_5 coatings obtained at different oxidation temperatures, optical spectroscopy was performed on individual samples at room temperature. THR spectra shown Fig. 2 (a) indicate that the oxidation temperature has a significant impact on the wavelength at which a reflection plateau is observed. An apparent red shift is observed with the increased in oxidation temperatures. This observation concurs with the variation in colours noticed after the post oxidative treatments.

The brightness of the coating can be defined as the total integrated THR (area under the curve) over the full range of visible spectrum (400–800 nm). Therefore, from Fig. 2 (a) we observe that V_2O_5 coatings obtained by oxidation at 450 °C are brighter compared to the films oxidised at 350 °C and 550 °C. The graph showing the variation of brightness with respect to oxidation temperature is show in Fig. 2 of ref [36]. Fig. 2(b) correlates the brightness of the films to their texture. It is evidenced that brightness varies linearly with $I_{(200)}/I_{(001)}$, indicating that coatings that are highly oriented to (001) direction exhibit lower brightness compared to polycrystalline samples. No obvious explanation could be postulated for this undoubtful brightness to texture correlation.

V_2O_5 has a layered structure with a large affinity towards accommodating guest molecules between the interlayer spaces. This property of V_2O_5 has made it an ideal candidate for many applications like gas and humidity sensing [37], energy storage [38] and catalysis [39]. In order to prove that thermochromism in V_2O_5 is an intrinsic property, and that it does not depend on the atmospheric conditions, we isolated the coatings from ambient atmosphere. The passivation was performed using the established Atomic Layer Deposition (ALD) of Al_2O_3 [40,41]. ALD coatings offer superior advantages compared to other deposition techniques by allowing low temperature of deposition and a conformal coating characteristics. All the samples were coated with a 20 nm of Al_2O_3 oxide. In addition to encapsulation, Al_2O_3 would also act as a protection layer by making V_2O_5 scratch resistant and prevent from aging via a change of the oxygen deficiency.

The optical band gap E_g was calculated as a function of temperature using the temperature dependent THR spectra, by Tauc's equation, $\alpha hv = B(hv - E_g)^r$. Where, α is absorption coefficient, E_g = the optical energy gap of the film, B = a constant, $h\nu$ = the incident photon energy and r is a numeric value equal to 1/2 for allowed direct transitions and 2 for allowed indirect transitions. The optical energy gap is estimated by plotting $(\alpha hv)^{1/r}$ versus $(h\nu)$, then interpolating the straight line to the photon energy axis at the value $(\alpha hv)^{1/r} = 0$. The optical data for vanadium pentaoxide films

were found to give a better fit for the exponent $r = 1/2$ confirming the direct allowed nature of the involved transition. Fig. 2(c) shows the variation of the optical band gap at room temperature with respect to the oxidation temperature for both pristine and Al_2O_3 deposited V_2O_5 coatings. Similar to the THR, Al_2O_3 deposition has no significant impact in the band gap values. The optical band gap decreases from 2.26 to 1.8 by increasing the oxidation temperature. The reason for this variation can be associated with the oxygen deficiency in the film.

Optical properties of Al_2O_3 coated samples showed no significant deviation from those of pure coatings. Therefore those results are not presented here. Henceforth all the data reported in this article correspond to V_2O_5 coatings with an Al_2O_3 encapsulation. V_2O_5 coatings oxidised 350°C-550 °C exhibited visible range thermochromism. Whereas coatings oxidised at 580 °C do not show any sign of thermochromism. The brightness and the extent of red shift vary considerably depending on the temperature at which post deposition oxidative annealing was performed. First derivative curves of temperature-dependent optical spectra of samples oxidised at 350 °C, 450 °C and 550 °C are shown in Fig. 3 (a), (b) and (c) respectively. On heating the samples from RT to 250 °C, a red shift is observed with a slight decrease in the brightness of the coatings. The insets in each panel of Fig. 3 show the photographic images of V_2O_5 coatings at RT and at elevated temperature respectively. Fig. 3 in Ref. [36] shows the temperature dependent optical spectra of V_2O_5 coatings oxidised at various temperatures.

The colour of V_2O_5 returned to its room temperature state on cooling, evidencing a perfectly reversible nature of this thermochromism. It should be noted that thermochromism under ambient air is measured at temperatures that are significantly lower than the respective oxidation temperatures. Blue and red vertical dotted lines in Fig. 3 provide a visual guide to inform about the spectral range concerned by thermochromism for each sample.

Besides the thermochromism that occurs with an impressive change in colour, total brightness of the sample, which can be described as the integrated reflection over the whole range of visible spectrum, decreases as a function of temperature. The rate of decrease in brightness can be equated to the sensitivity of V_2O_5 to temperature changes. Fig. 4 shows the variation of brightness with increasing oxidation temperature for the three samples. We observe a linear decrease in the brightness for all samples.

The sensitivity of the thermochromic coating is defined here as the slope of the linear fitting of the brightness versus temperature curve. From Fig. 4, slope of V_2O_5 coatings obtained by oxidation at

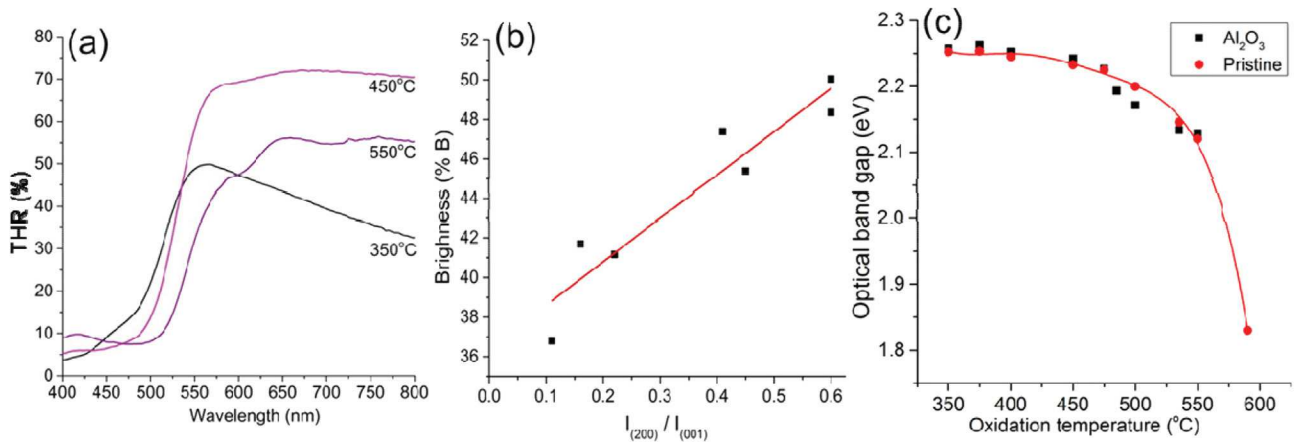


Fig. 2. (a) Room temperature THR spectra of samples oxidised at 350, 450 and 550 °C. (b) Dependence of the brightness of the coatings with the ratio of XRD intensity I_{200}/I_{001} and (c) the variation of optical energy band gap as a function of oxidation temperature for both pristine V_2O_5 as well as Al_2O_3 coated V_2O_5 .

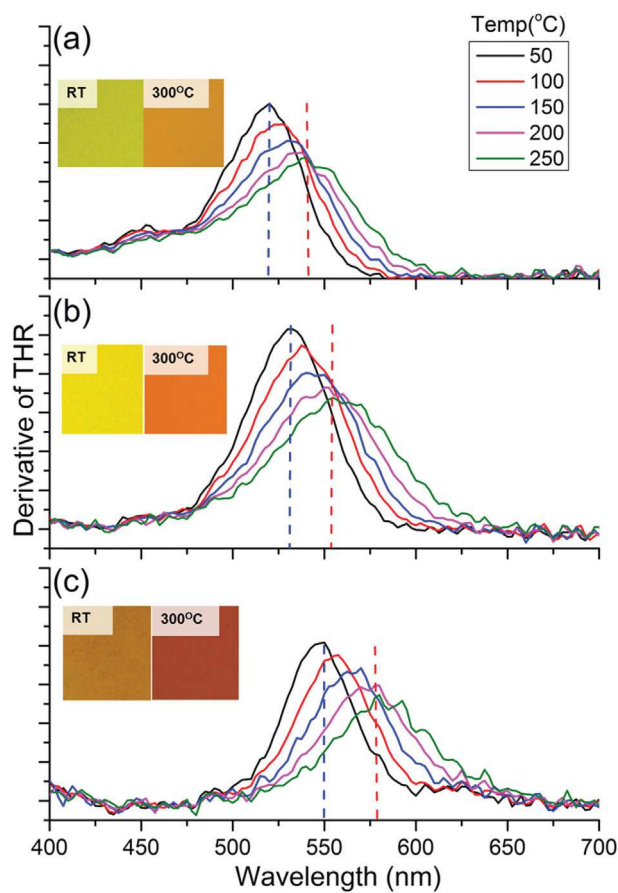


Fig. 3. Temperature-dependent $\frac{d(THR)}{d\lambda}$, demonstrating thermochromic behaviour of samples oxidised at (a) 350 °C, (b) 450 °C and (c) 550 °C respectively. Inset for each panel displays the photographic image of V_2O_5 coatings at room temperature and 300 °C respective to each oxidation temperature.

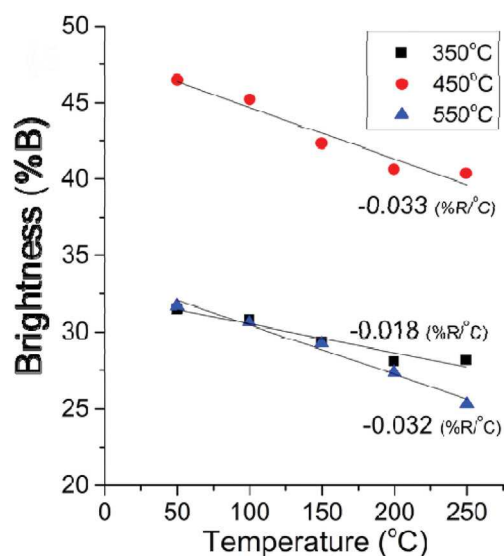


Fig. 4. Variation of brightness as a function of temperature for V_2O_5 obtained by oxidation at 350 °C, 450 °C and 550 °C.

350 °C, 450 °C and 550 °C is 0.018, 0.033 and 0.032 $\Delta\%R/^\circ C$. Hence samples obtained by oxidation at 450 °C and 550 °C feature a similar sensitivity and are almost twice as much sensitive to

temperature changes compared to the one obtained by oxidation at 350 °C. Since the sensitivity is measured taking into account the variation in brightness, the quantified sensitivity value are quite low as brightness is calculated over the full visible spectrum. However, if the sensitivity is measured as the variation in THR for a particular wavelength (e.g. $\lambda = 535, 555$ and 575 nm) as shown data in brief, we notice a one order of magnitude higher thermochromic sensitivity.

With the ability to showcase precise and accurate changes in optical properties, which respond to temperature changes, these thermochromic V_2O_5 coatings could be ideal candidates to operate as a contactless optical temperature sensor. The range and variation of colours observed further strengthen the versatility and tunability aspects of these V_2O_5 coatings. Through controlled oxidative annealing we obtain thermochromic coatings with adjusted colours and varying sensitivity to the temperature stimulus.

The high susceptibility of V_2O_5 to undergo reduction under ultra-high vacuum with X-rays or electron beam exposure complicates its quantitative analysis [42,43]. Therefore analysis conditions as those encountered in EDX and XPS, reduce V_2O_5 to immediate lower oxides of vanadium such as V_6O_{13} [44] creating hurdles in accurate determination of vanadium and oxygen ratios.

Controlled oxidation of as-grown films to V_2O_5 is accepted to yield films with various oxygen deficiencies [45,46]. These oxygen deficiencies are assumed to be responsible for the wide range of reported optical band gaps [47] and perceived colours [35]. We present tunable thermochromic V_2O_5 coatings, achieved by controlled oxidative annealing. In addition, Al_2O_3 encapsulation prevents change of the oxygen vacancies in the film during extended periods of operation at elevated temperatures, without impacting the thermochromic properties.

4. Conclusions

Pure single phase V_2O_5 coatings were obtained by controlled oxidation of VOx films deposited using DLI MOCVD. Reversible visible thermochromism was observed upon heating under ambient atmosphere. The colour of thermochromic V_2O_5 could be adjusted by controlling the synthesis conditions. XRD reveals a pure phase polycrystalline nature of the coatings. Temperature-dependent optical spectroscopy for samples obtained by oxidation at 350 °C, 450 °C and 550 °C confirm that each sample has a different window of thermochromic transition. Therefore, tuning the thermochromic behaviour is effectively achieved by controlling the oxidative annealing that enables adjusting the oxygen deficiency. Films oxidised at 580 °C were not thermochromic, indicating that thermochromism is directly related to the oxygen deficiency. Hence it was shown that controlled oxygen vacancy plays a key role in expressing new functionalities of transitional metal oxides and V_2O_5 in particular.

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