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Tunable thermochromic properties of V_2O_5 coatings

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ABSTRACT

Thermochromic Di vanadium pentaoxide (V_2O_5) 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 V_2O_5, allows tuning the colour of the films and as a consequence its thermochromic behaviour. Non oxygen deficient V_2O_5 did not feature any measurable thermochromism

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 (Cr_2O_3), 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 V_2O_5 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 V_2O_5 coatings, to achieve fine control over the perceived colour and thermally induced colour change.

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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 form 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 CuKα as the X-ray source. Data were collected in the θ-2θ (locked couple) mode from 2θ 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^{o}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].

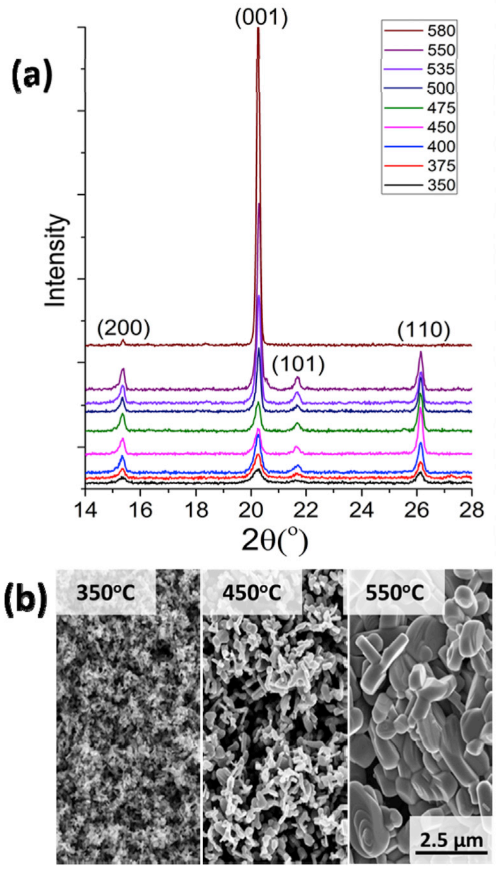

Fig. 1. (a) X-Ray diffractograms of V_2O_5 films oxidised at different temperatures reveal formation of pure, single phase orthorhombic structure as per PDF no [000411426] and (b) surface scanning electron micrographs of the oxidised films at 350 °C, 450 °C and 550 °C.