

Vanadium oxides prepared by liquid injection MOCVD using vanadyl acetylacetonate

D. Vernardou*, M.E. Pemble¹, D.W. Sheel

Institute for Materials Research, University of Salford, Cockcroft Building, Salford, Manchester, M5 4WT, UK

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Abstract

Atmospheric pressure liquid injection MOCVD was used for the deposition of vanadium oxide coatings using vanadyl acetylacetonate as precursor in methanol solution. The deposition was carried out on SiO₂-precoated glass using oxygen flow rates of 0, 0.02, 0.04, 0.06 and 0.08 L/min over the temperature range 375–450 °C. For growth at the highest temperatures studied, which gave the best results in terms of film crystallinity, the influence of oxygen flow rate on the degree of crystallinity, microstructure and morphology of the films was studied in detail. The films were characterized by X-ray diffraction, IR reflectance-transmittance, Raman microscopy and scanning electron microscopy. Results obtained demonstrate the thermochromic properties of vanadium oxide films at a switching temperature at 60 °C together with the fact that liquid injection MOCVD is an efficient method of producing vanadium dioxide using vanadyl acetylacetonate as precursor. The capability to control the microstructure and properties of VO₂ films grown on SiO₂-precoated glass by altering the process parameters can be significant for certain practical applications of thermochromic coatings, such as ‘smart windows’.

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1. Introduction

Vanadium dioxide undergoes a well-known reversible semiconductor-to-metal transition at 68 °C, accompanied by a crystallographic transformation from a monoclinic structure, VO₂ (M), to the tetragonal rutile structure, VO₂ [1]. This class of material is considered interesting because it shows a large variation of optical and electrical properties with temperature, thus making materials such as VO₂ candidates for applications involving electrical or optical switching elements (memory devices) [2]. The semiconductor-to-metal transition temperature in VO₂ can be lowered further by doping with ions such as tungsten, molybdenum or niobium [3–5]. In VO₂, the phase transition is such that this material can be used in the design and fabrication of ‘smart windows’ for buildings so that efficient use can be made of the incident solar radiation [2]. Vanadium oxides including VO₂ have been made in many ways including sol-

gel techniques [6], vacuum evaporation [7] as well as chemical methods [8,9] and most recently chemical vapour deposition (CVD) [10].

To date, direct liquid injection metal organic chemical vapour deposition (DLI-MOCVD) has not been reported for the production of vanadium oxide thin films. The liquid injection MOCVD route potentially provides the most flexible means of producing thin films with a high degree of control of stoichiometry, crystallinity and uniformity, while also permitting the use of precursors with low volatility. In this present work, we present data for the growth of VO₂ thin films from a metal organic precursor, vanadyl acetylacetonate, using liquid injection CVD, which demonstrate the ability to grow VO₂ films, which exhibit well-defined thermochromic behaviour. To the best of our knowledge, this is the first report of such a process.

2. Experimental

The liquid injection MOCVD system employed in the growth of the films was performed on a custom-built

* Corresponding author. Tel.: +44 1612954800; fax: +44 1612955111.

E-mail address: d.vernardou@hotmail.com (D. Vernardou).

¹ Present address: NMRC, Lee Maltings, Prospect Row, Cork, Ireland.

apparatus described in detail elsewhere [11]. Briefly, this consists of a horizontal atmospheric pressure reactor system (Electrogas Systems) equipped with a syringe-driven injection system, heated inlet lines and a vapouriser designed to encourage evaporation of the solvent used in the precursor solution. A solution of 0.1 mol dm^{-3} of vanadyl acetylacetonate (99%, Aldrich, UK) in methanol was placed into a syringe driver. The solution was injected into the plain line gas-flow using a fixed rate of 3 ml/h. High-purity (99.99%) argon gas was used as the system gas in all reactions, while high-purity (99.995%) oxygen gas, which acts as the oxidant, was fed into the reactor through a separate gas line. Electronic mass flow controllers were used to regulate the flow of both gases. A capacitance manometer was used to measure the total pressure in the reactor. The CVD process was conducted at a total pressure of 1 atm. Thin films were deposited on SiO_2 -precoated glass of dimensions $2 \times 1 \text{ cm}$ (Pilkington Glass, UK). Substrates were cleaned in acetone, methanol, ethanol and deionised water and then allowed to dry in air.

A series of films was prepared by varying the oxygen flow rate from 0, 0.02, 0.04, 0.06 and 0.08 L/min over the temperature range $375\text{--}450 \text{ }^\circ\text{C}$. The precursor transport lines were heated to $150 \text{ }^\circ\text{C}$ to enhance transport of precursor solution and to prevent condensation in the lines.

X-ray diffraction measurements were performed using a Siemens D5000 Diffractometer under specific operating conditions: 40 kV, 40 mA for $2\theta=20.000\text{--}55.000$, step size 0.1° and time step 30 s per degree, with a glancing angle of 2° . All peak positions and diffraction intensities were matched with database spectra. The spectral transmittance in normal incidence and the spectral reflectance in 30° incidence angle and S polarisation in IR region were measured using an NKD 6000 spectrophotometer at 25 and $65 \text{ }^\circ\text{C}$, using a designated heating stage. Transmittance-temperature studies were performed on a Perkin-Elmer 457

grating spectrometer set to 4000 cm^{-1} . An aluminium temperature cell controlled by RS heaters, Eurotherm temperature controllers and K-type thermocouples was used to control sample temperature. Sample temperature was measured by a K-type thermocouple taped to the film surface. Temperature-dependent Raman measurements were performed using a Renishaw 1000 spectrometer together with a 632.8-nm laser operating at 2-mW power and $50\times$ magnification. In this arrangement, the sample temperature was controlled by a Linkam THMS600 variable temperature cell. Raman measurements were made using the following experimental parameters: wave number range $150\text{--}750 \text{ cm}^{-1}$, power 25%, 50 accumulations and 10 s per accumulation. Scanning electron microscopy (SEM) was performed on a Jeol JEM-100CX electron microscope. Samples for SEM analysis were overcoated with a thin film of gold to make them more conductive.

3. Results and discussion

Films deposited at 0, 0.02, 0.04, 0.06 and 0.08 L/min oxygen flow rates over the temperature range $375\text{--}450 \text{ }^\circ\text{C}$ were found to be variable in terms of crystallinity, uniformity and visual appearance. In general, it was found that the degree of preferred oxide (VO_2) phase and crystallographic orientation was greater when the growth temperatures were higher, for the range of oxygen flow rates employed, presumably due to the greater mobility of the growth species. For this reason, the data presented here all refer to a growth temperature of $450 \text{ }^\circ\text{C}$.

Fig. 1 shows the XRD patterns of the various films grown over the range of oxygen flow rates at $450 \text{ }^\circ\text{C}$ on SiO_2 -precoated glass. From Fig. 1, it may be seen that for the samples grown in the absence of any oxygen flow, three distinct peaks are observed in the diffractogram at 2θ values

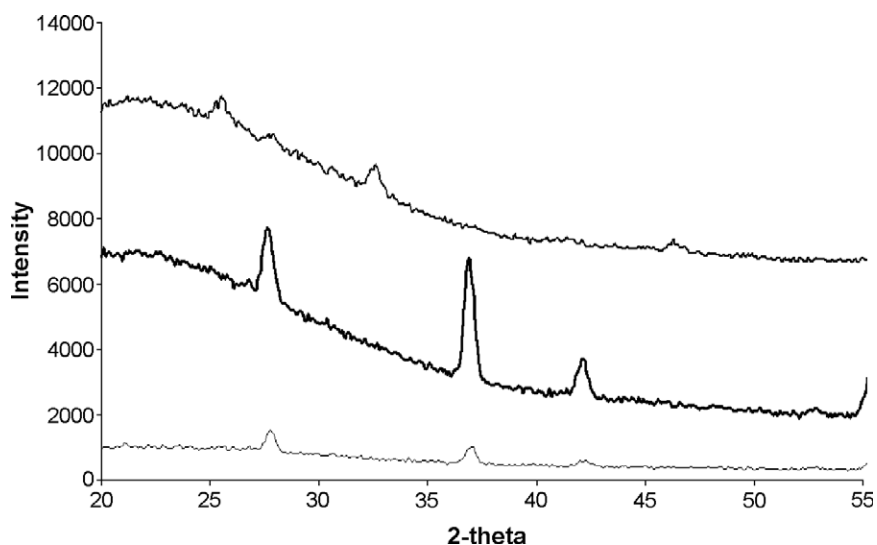


Fig. 1. X-ray diffraction analysis of —: 0 L/min, —: 0.02 L/min and —: 0.04 L/min oxygen pressures at $450 \text{ }^\circ\text{C}$ on SiO_2 -precoated glass.

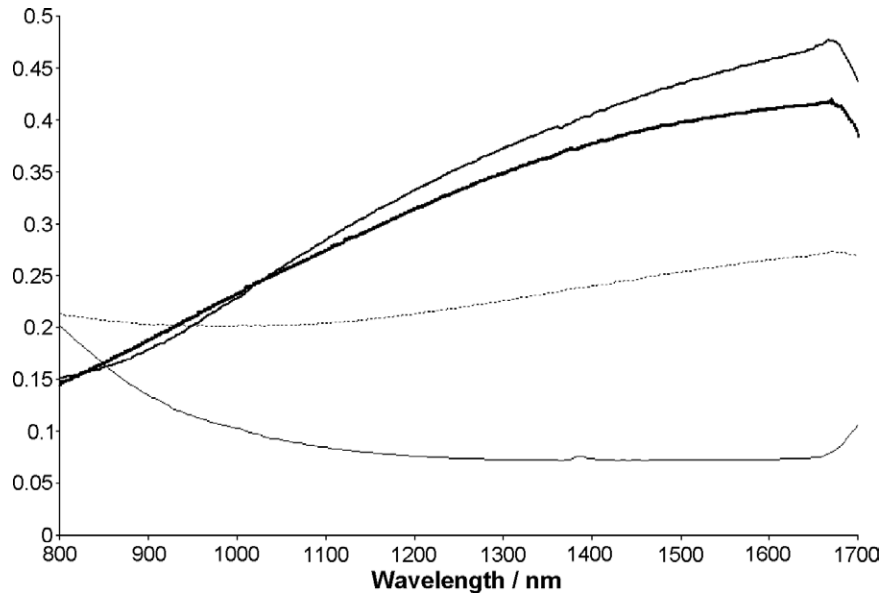


Fig. 2. Transmittance-reflectance spectra of vanadium oxide thin film under 0.98 L/min Ar and 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass, at 25 and 65 °C, illustrating the thermochromic properties. - -: Transmittance at 25 °C; —: transmittance at 65 °C; -·-·: reflectance at 25 °C; - - -: reflectance at 65 °C.

and respective miller indices of 25.6° (100), 32.6° (110) and 46.3° (111), which, by comparison with the literature database, suggests the existence of crystalline V₂O₅. In contrast, the X-ray diffractograms for samples grown using oxygen flow rates of 0.02 and 0.04 L/min show three peaks at 2θ values and respective miller indices of 27.7° (100), 36.9° (110) and 42.2° (110), consistent with the formation of VO₂.

Fig. 2 shows the spectral transmittance and the spectral reflectance of the samples grown on SiO₂-precoated glass at 450 °C using 0.98 L/min Ar and 0.02 L/min O₂, over the range 800–1700 nm, recorded at 25 and 65 °C. As one may

observe, the films display the basic properties required for intelligent window-coating applications, in the form of general IR transmittance and reflectance characteristics that would be desirable in terms of the control of solar radiation, i.e., increased reflectance (reduced transmittance) in the spectral region 800–1700 nm.

The optical constants were determined from the measured transmittance and reflectance at 25 and 65 °C using the Cauchy model [12]. For the film deposited using 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass for the region 800–1700 nm, there was a significant transition change of refractive index from the value calculated for 25 °C (2.4) to

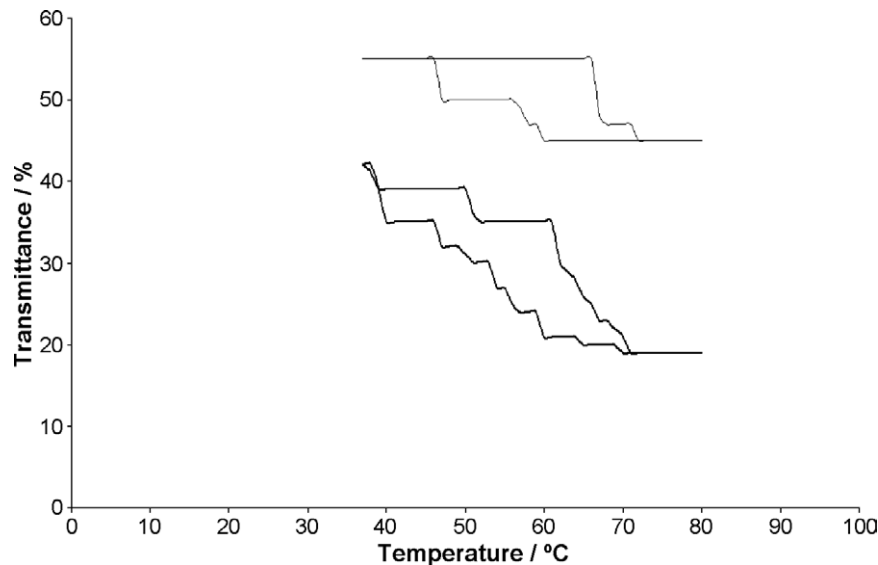


Fig. 3. Transmittance at 2.5 μm against temperature for film deposited under —: 0.96 L/min Ar, 0.04 L/min O₂ and - -: 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass.

the value calculated for 65 °C (1.3) at a wavelength of 1300 nm. Similarly, the calculated absorption coefficients showed a change, from 0.48 at 25 °C to 1.4 at 65 °C, indicating the transition to the metallic state. These values are in good agreement with values obtained by other researchers [13].

The thermochromic transition temperatures for the films grown on SiO₂-precoated glass at 450 °C were also monitored by studying the change in transmittance at 2.5 μm. The sample temperature was increased by 2 °C/min until no further change in transmittance was observed and then allowed to cool to room temperature. Results of this study for films deposited under conditions 0.96 L/min Ar, 0.04 L/min O₂ and 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C are shown in Fig. 3. The transition temperature was taken to be at the centre of the hysteresis loop, while the width of the hysteresis loop was also recorded as being of interest in terms of defining the sharpness of the transition. For the two experiments concerned, the transition temperatures and hysteresis loop widths are, respectively, 62.5 and 15 °C for 0.04 L/min O₂ flow rate and 60 and 9 °C for 0.02 L/min O₂ flow rate.

In order to observe the phase change during the thermochromic transition directly by Raman microscopy, a heating cell was used to raise the temperature of the films on the SiO₂-precoated glass substrates at a rate of 2 °C/min. The temperature was allowed to stabilize at the chosen temperature for 10 min before the spectrum was obtained. A typical set of VO₂ spectra for 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C recorded at 25, 50 and 65 °C and cooling back to 25 °C from 65 °C is shown in Fig. 4. From Fig. 4, it may be seen that as the temperature of the film was increased, the Raman bands for the monoclinic phase of VO₂ are seen to decrease in intensity until the monoclinic VO₂ bands are no longer visibly observed. On cooling, the Raman bands for VO₂ are again observed illustrating the reversible nature of the transition.

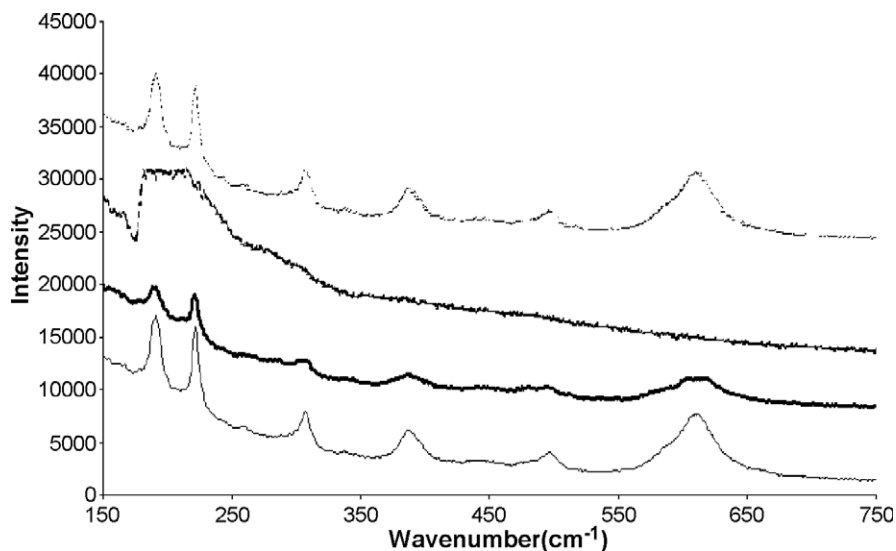


Fig. 4. Raman spectra on film deposited under 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass at —: 25 °C, - - : 50 °C and ···: 65 °C, cooling back to - · - : 25 °C from 65 °C.

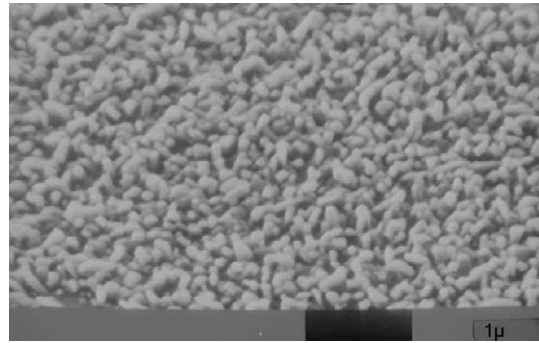


Fig. 5. SEM image of vanadium oxide deposited under 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass. The line equals 1 μm.

An SEM micrograph of vanadium oxide deposited under 0.98 L/min Ar, 0.02 L/min O₂ at 450 °C on SiO₂-precoated glass is shown in Fig. 5, which reveals that the film consists of well-formed crystallites. As one can see, the grains are uniform in size and morphology. At this stage, it is proposed that the films are coherent and increase in roughness as the film thickness increases. However, more data are required in order to be able to comment definitively on the nature of the growth process, and thus, it is also possible that the film appearance results from incoherent island growth.

4. Conclusions

Liquid injection CVD has been used for the first time with vanadyl acetylacetonate to grow thin films of vanadium oxides on SiO₂-precoated glass over a range of temperatures and oxygen flow rates. The most crystalline films were produced at the highest temperature studied, 450 °C. The addition of an oxygen flow appears to induce the growth of VO₂. Spectrophotometry measure-

ments have revealed the thermochromic nature of some of the films produced. The thermochromic transition temperature measurements show that films grown at the higher oxygen flow rate employed show poorer transition characteristics in terms of sharpness, i.e., larger hysteresis loops. Transition temperatures were also slightly higher, although the differences here remain to be established via the study of a wider range of samples. Raman spectroscopy measurements indicate that there is a transition temperature below 65 °C. Finally, the SEM micrographs of the films indicate that the crystallites are well formed and the grains are uniform in size and morphology. The capability to control the crystallinity and properties of vanadium dioxide films grown on SiO₂-precoated glass by altering the process parameters in liquid injection MOCVD has been demonstrated here. Such control may be significant for the production of ‘smart windows’ and related applications.

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