



Thermochromic vanadium dioxide thin films from electric field assisted aerosol assisted chemical vapour deposition

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ABSTRACT

Thermochromic vanadium dioxide thin films were deposited via aerosol assisted chemical vapour deposition from a precursor solution of vanadyl acetylacetonate in ethanol at 525 °C on to fluorine doped tin oxide coated glass substrates. A potential difference was applied between the top plate and substrate during the deposition to generate an electric field with a positive bias applied to the substrate. The films produced were analysed and characterised by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, contact angle and variable temperature UV/Visible spectroscopy. It was found that the presence of an electric field during deposition could lead to a marked change in the microstructure and functional properties of the deposited films; specifically the wetting and thermochromic properties. An increase in field strength lead to a reduction in crystallite and agglomerate size compared to films grown without the presence of an electric field.

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1. Introduction

In recent years there has been much interest in thin films of vanadium (IV) oxide (VO₂) for use in intelligent glazing systems. [1,2] The interest stems from the inherent thermochromic transition which VO₂ undergoes causing a transition between semiconductor and metallic properties, occurring at 68 °C for pure single crystals [3]. The transition is due to a structural change from the low temperature monoclinic phase (VO₂ M) to the high temperature rutile phase (VO₂ R). [4] This change results in a significant change in optical and electrical properties. The low temperature VO₂ M phase is semiconducting and transmits a wide range of solar radiation. In contrast the high temperature VO₂ R is metallic and far more reflective to solar radiation especially that in the *infrared* region.

This transition and accompanying properties makes VO₂ an interesting candidate for variable temperature heat mirror there are still some problems which need to be addressed before it could be considered viable. The main concern for this technology is the high temperature at which the transition occurs and how this could be reduced [5]. The ideal temperature for the transition is thought to be between 20 and 30 °C although this will vary depending on the environment in which it is going to be used [5–7].

Previous investigations into the use of dopants have shown some success in reducing the transition temperature. The dopants that have been found to effectively lower the transition temperature are high valence metal ions. The most effective of these ions is tungsten, which has been the subject of significant investigation showing that dopant levels ~2 at% can drop the transition temperature ~25 °C [8]. This does however lead to a reduction in the variation of the infrared optical properties associated with the transition.

It has also been seen that a reduction in film thickness also leads to a reduction in the transition temperature [6]. This decrease in transition temperature is thought to occur as a result of an increase of strain within the film [9]. There has also been work done that shows a correlation between deposited particle size reduction and a reduction in transition temperature [10]. It is the reduction of particle size that this paper will report on.

It has been previously reported that applied electric fields during CVD reactions can cause a decrease in particulate size as well as some variation in orientation and growth preference [11–14]. In this paper we report on the use of electric fields in the growth of VO₂ thin films with a continual positive bias applied to the substrate.

2. Experimental section

Reactions were carried out in a quartz cold walled reactor set up as shown in Fig. 1. A 0.1 M solution of [VO(acac)₂] (Aldrich 99.99%) was made up by dissolving 0.384 g in 15 ml of ethanol. The solutions were stirred for 20 min prior to use to ensure the [VO(acac)₂] had dissolved

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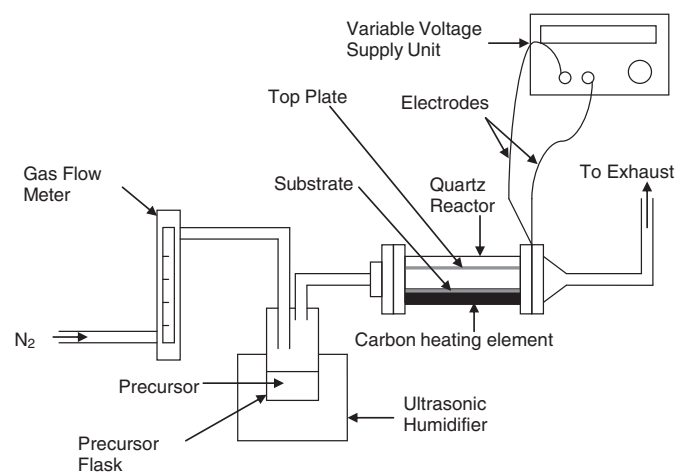


Fig. 1. Schematic diagram illustrating the set up of electric field assisted chemical vapour deposition.

fully. The precursor aerosol was formed using a Vicks ultra sonic humidifier and observing a mist before diverting to the reaction chamber using nitrogen (BOC, 99.99%) as a carrier gas. This aerosol assisted chemical vapour deposition process has been shown to produce V_2O_3 , VO_2 and V_2O_5 depending on flow rate and reactor temperature. For these set of experiments the flow rate was set to 2 L min^{-1} and the reaction chamber was heated to 530°C using a graphite block containing a Whatman heating cartridge, with temperature gradients of up to 100°C between the top plate and the substrate. The substrate temperature was monitored using Pt-Rh thermocouples. The substrate and top plate were glass sheets ($90 \text{ mm} \times 45 \text{ mm} \times 4 \text{ mm}$) with a fluorine doped tin oxide transparent conducting oxide layer. A potential difference was applied between the top plate and substrate with a DC voltage with positive bias on the substrate. The top plate and substrate were separated by 1 cm allowing the precursor and carrier gas to pass between them. Thin sheets of alumina were used to stop short circuiting between the electrodes and the reaction chamber.

The samples were cut into $1 \text{ cm} \times 1 \text{ cm}$ pieces and used for analysis. Energy dispersive analysis of X-rays (EDAX) and wavelength dispersive analysis of X-rays were conducted using a Phillips XL30 ESEM instrument. Scanning electron microscopy (SEM) images were acquired on a Jeol 6301 F field emission instrument. X-ray diffraction patterns were measured on using monochromated ($\text{CuK}\alpha_{1+2}$) radiation in the reflection mode using a glancing incident angle 5° . Raman spectra were acquired on a Renishaw Raman system 1000 using a helium-neon laser of wavelength 632.8 nm . The Raman system was calibrated against the emission lines of neon. High resolution X-ray photoelectron spectroscopy (XPS) was performed using a Thermo photoelectron spectrometer using monochromatic $\text{Al-K}\alpha$ radiation. Survey spectra were collected at a pass energy of 160 eV , whilst narrow scans were acquired at a pass energy of 40 eV . The data was analysed using CasaXPSTM software and calibrated to the $\text{C}(1 \text{ s})$ signal at 284.1 eV , attributed to adventitious carbon. Ultraviolet / visible (UV/Vis) spectroscopy was conducted on a Perkin Elmer Lambda 950 instrument. Contact angles were measured with a FTÅ 1000 B Class instrument.

3. Results and discussion

The films yielded from the electric field assisted chemical vapour deposition (EACVD) reaction of vanadyl acetylacetonate in ethanol at 530°C onto a glass substrate afforded yellow/brown films. The films were adherent to the surface and could not be wiped off with paper towel, passed the scotch tape test and could not be marked

by a brass stylus. They could however be removed using a steel stylus. The growth conditions and analysis are summarised in Table 1.

EDAX spot analysis confirmed the presence of both vanadium and oxygen in the films and indicated that no other element was present above the limit of detection of the machine ($\sim 0.5 \text{ at.}\%$).

The SEM images show that the application of an electric field had dramatic effect on the micro-structure of the deposited film. Fig. 2A shows the films which were produced without application of an electric field. These films have a similar appearance to previously reported films of vanadium oxide produced by the aerosol assisted chemical vapour deposition route [8]. These films show a surface composed of agglomerates of $50\text{--}100 \text{ nm}$ in diameter with a high coverage. The application 200 Vm^{-1} electric field (Fig. 2B) caused a change in film structure leading to the appearance of larger islands ($200\text{--}300 \text{ nm}$ diameter) formed of much smaller agglomerates ($15\text{--}20 \text{ nm}$ diameter) giving a shrub like appearance. The film also appears to have more complex surface topology displaying a pseudo dendritic growth with a more porous surface. The application of a 500 Vm^{-2} (Fig. 2C) further increased the effect of the complexity of the surface topology giving a more porous appearance with the agglomerate size further reducing ($5\text{--}10 \text{ nm}$ diameter) and greater micro structure complexity being observed. This trend in micro structure variation is seen to continue with the further increase in electric field strength 1500 Vm^{-1} (Fig. 2D) the size of agglomerates does not appear to further decrease although the larger shrub like islands that were observed have coalesced to form a complex surface with the shrub like features being largely obscured. At the highest strength field, 3000 Vm^{-1} (Fig. 2E) the slight appearance of the larger islands is now non observable and the small agglomerates cover the whole surface yielding a film with complex surface structure and topography.

The contact angles observed (Table 1) for the films are reduced as the applied electric field strength during the deposition is increased. This is attributed to the change in microstructure and increasing surface roughness that can be observed in the SEM images (Fig. 2A–E).

X-ray diffraction of sample A (Fig. 3) showed that the prevalent phase was monoclinic vanadium dioxide with a space group of $C 1 2/m 1(12)$ (PDF# 01-076-0673 33-1441). The application of an electric field led to a change in crystallographic space group compared to the plain aerosol assisted CVD produced film (sample A), a space group of $P 1 21/c 1(14)$ (PDF# 01-076-0456 43-1051) is noted. 011, 310 and 220 peaks are observed and the 201, 200 and 210 peaks disappear. As electric field strength used in the deposition increased the 011, 310 and 220 peaks was seen to shift to lower values of 2θ (Fig. 3B–E). This is indicative of a reduction in unit cell volume, although we have not evaluated this numerically as the XRD data obtained thus far, is not of high enough quality for a definitive answer to be produced. Peak broadening was also observed for the EACVD samples (B–E), compared to plain aerosol assisted CVD sample. This is indicative of a decrease in crystallite size, the extent of which was similar for all films produced using the EACVD method.

Raman spectroscopy (Fig. 4) confirmed the presence of both VO_2 and V_2O_5 on the surface of the deposited film. Samples produced with higher electric fields (samples D and E) were poor Raman scatterers. This is attributed to the decrease in crystallite size and subsequent surface roughening (Fig. 2). Raman scattering also confirmed the presence of graphitic carbon with two broad peaks catered around 1100 and 1400 cm^{-1} in all samples (not shown).

X-ray photoelectron spectroscopy of the film surface (Fig. 5) indicated multiple vanadium and oxygen environments for all of the samples examined. Modelled vanadium shifts ($V 2p_{3/2}$) of 516.8 , and 517.8 eV are consistent with those previously reported for, VO_2 , and V_2O_5 , respectively [7]. The $O 1 \text{ s}$ peak is centred at 530.9 eV and is quite broad and asymmetric, indicating more than one oxygen environment is present, consistent with multiple vanadium oxide environments and likely containing a shift due to absorbed water. Previous work has reported the presence of fully oxidized vanadium at the surface [11], as such the observation of multiple vanadium environments is not

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