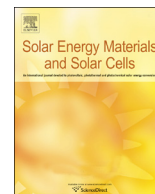




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# Thermochromic vanadium dioxide thin films from electric field assisted aerosol assisted chemical vapour deposition

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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 improved wetting and thermochromic properties. An increase in field strength lead to a reduction in crystallite and agglomerate size and an increase in near infrared transmission 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 (VO<sub>2</sub>) for use in intelligent glazing systems [1–3]. The interest stems from the inherent thermochromic transition, which VO<sub>2</sub> under goes causing a transition between semi conductor and metallic properties, occurring at 68 °C for pure single crystals [4]. The transition is due to a structural change from the low temperature monoclinic phase (VO<sub>2</sub> M) to the high temperature rutile phase (VO<sub>2</sub> R) [4]. This change results in a significant change in optical and electrical properties. The low temperature VO<sub>2</sub> M phase is semiconducting and is transmissive a wide range of solar radiation where as the high temperature VO<sub>2</sub> R is metallic and far more reflective to solar radiation especially that in the *infrared* region.

This transition and accompanying properties makes VO<sub>2</sub> 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 [6–8].

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 valance metal ions. The most effective of these ions is tungsten and has been the subject of some investigation showing that dopant levels ~2 at% can drop the transition temperature ~25 °C [9,10]. 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 [11]. It is thought that this is caused by an increase in film strain [12]. There has also been work done that shows a correlation between deposited particle size reduction and a reduction in transition temperature [13].

Aerosol assisted CVD (AACVD) is a widely used technique for the production of thin films. The AACVD method differs from the standard CVD technique by using an aerosol of precursor liquid rather than a vaporised precursor. This use of aerosols allows a wider range of precursors to be employed because the limiting factor is solubility rather than volatility. It also allows the use of less stable precursors as there is no longer a heating requirement to get them into the gas phase.

AACVD has been used in previous studies for the production of various vanadium oxides, V<sub>2</sub>O<sub>3</sub>, VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, on glass [14]. In this study vanadium oxides were deposited from dissolved [VO(acac)<sub>2</sub>] or [V(acac)<sub>3</sub>]. The mix of oxides was controlled using different solvents, precursor flow rates and substrate temperatures. Variation

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of these factors was found to allow for good control of the deposited materials. The work studied a group of different solvents for the AACVD reaction. The solvents used were a mix of methanol and water at varying ratios, or ethanol. The water–methanol solvents produced only  $V_2O_3$  (karelianite) while ethanol could produce  $VO_2$  or  $V_2O_5$ . Other solvents were also used in the work, acetone, acetonitrile and ethyl acetate. These however were reported to produce black powdery films with no discernable XRD patterns. The higher precursor flow rates were found to produce films with greater oxidation states. This was attributed to the increase in oxygen in the reaction chamber due to more rapid decomposition of the solvent on entering the reaction chamber. The only route found to produce pure  $VO_2$  (M) was that with  $[VO(acac)_2]$  in ethanol. The reaction temperature could be varied between 500 and 600 °C without causing effect on the deposited film. The work concludes that the deposition process is affected by a combination of gas phase fluid dynamics and surface oxidation chemistry. Both gas phase fluid dynamic and surface oxidation chemistry might be affected by the presence of an applied electric field.

The AACVD technique has also been applied to the production of doped vanadium dioxide thin films with the aim of reducing the transition temperature. The most effective dopant has found to be tungsten. Doped films can be deposited using a single solution of  $[VO(acac)_2]$  and  $[W(OC_2H_5)_5]$  in ethanol. This method was used to deposit up to 2% atom with a linear relationship between the precursor ratio and the ratio in the deposited film. The films showed a linear decrease in the transition temperature with increase in tungsten doping [10].

Similar work has also been carried out using AACVD to produce  $VO_2$  thin films doped with niobium, again with a view to reduce transition temperature. In that work  $[VO(acac)_2]$  and  $[Nb(OC_2H_5)_5]$  dissolved in ethanol were used as precursors. The concentration of Nb in the films was controlled by the concentration of  $[Nb(OC_2H_5)_5]$  in the solution while keeping  $[VO(acac)_2]$  concentration constant. This work found that the incorporation of Nb caused a reduction in the transition temperature but was less effective than the W doping requiring higher levels of doping to reduce the transition temperature to around 22 °C [15].

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 [16]. In this paper, we report on the use of electric fields in the growth of  $VO_2$  thin films and how this leads to changes in microstructure and functional properties.

## 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; and 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 AACVD 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  $2\text{ L min}^{-1}$  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 experimental set up has been reported in more detail previously [17].

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 6301F field emission instrument. X-ray diffraction patterns were measured on using monochromated ( $CuK_{\alpha 1+2}$ ) 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 on a Thermo monochromated aluminium  $K$ -alpha photoelectron spectrometer using monochromatic  $Al-K_{\alpha}$  radiation. Survey spectra were collected at pass energy of 160 eV, whilst narrow scans acquired at a pass energy of 40 eV. The data was analysed using CasaXPS™ software and calibrated to the  $C(1s)$  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.

A summary of the conditions used is shown in Table 1.

## 3. Results

All of the films produced were translucent brown, a colour indicative of  $VO_2$  films. The films could not be wiped away with blue towel, and passed the scotch tape test. The films could not be removed by a brass stylus but could be damaged using a steel stylus.

Fig. 1 shows the images of the thin films produced using EA (AA) CVD with varying strengths and type of applied field. The field strengths were varied between 0 and  $3000\text{ V m}^{-1}$ . All the images shown are at magnification of  $\times 20,000$ .

Fig. 1A shows a thin film where there was no applied field ( $0\text{ V m}^{-1}$ ). It can be seen from the SEM image that the surface morphology of the material is comprised of small globular islands of  $\sim 100\text{ nm}$  diameter with some joining to form larger islands of  $\sim 500\text{ nm}$  diameter. The surface shows no preferential growth direction and the surface appears relatively textured. This is comparable to previously observed results of similar AACVD reactions [10,14,15].

The first column of Fig. 1B–F shows the images of the films produced under increasing DC electric field strength with the bias of the electric field set such that the negative electrode was the substrate. For the weakest applied field (Fig. 1B,  $200\text{ V m}^{-1}$ ) it can be observed that there has already been some effect on the morphology when compared to the film without electric field (Fig. 1A). Fig. 1B shows that the presence of the field has caused a change in surface morphology. Worm-like or inverted-plate like structures with lengths  $\sim 500\text{ nm}$  and width of  $\sim 100\text{ nm}$  have appeared in the figure. These structures are formed of smaller agglomerated material with diameters of  $\leq 10\text{ nm}$ . The larger surface structure components are aligned randomly. When the field strength further increases to  $500\text{ V m}^{-1}$  (Fig. 1C), the surface has a rough complex appearance. This surface is a similar structure as in Fig. 1B with the difference being that the width of the worm-like features has decreased to  $\sim 10\text{ nm}$  while the lengths remain at  $\sim 500\text{ nm}$ . The surface worm-like structures are formed of smaller particles with diameters  $\leq 10\text{ nm}$ . An increase in the field strength to  $1500\text{ V m}^{-1}$  (Fig. 1D) causes a further decrease in the width of the worm-like features ( $\sim 5\text{ nm}$ ) giving them a nano-wire like appearance. It can also be seen that some of the larger islands have

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