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Electric field assisted aerosol assisted chemical vapor deposition of nanostructured metal oxide thin films

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ABSTRACT

Thin films of vanadium dioxide were deposited using a novel electric field assisted chemical vapor deposition methodology onto glass and gas sensor substrates. Electric fields were generated during the deposition reaction by applying a potential difference across the inter-digitated electrodes of the gas sensor substrate or buy applying an electric field between two transparent conducting oxide coated glass substrates. The deposited films were analyzed and characterized using scanning electron microscopy, Raman spectroscopy, X-ray diffraction, atomic force microscopy and contact angle measurements. It was found that applying an electric field led to large changes in film microstructure, preferential orientation and changes in the film growth rate. This led to significant changes in materials properties such as increased surface roughness and enhanced wetting behaviour. Electric field-assisted chemical vapour deposition shows great promise as a method for nano-structuring and tailoring the properties of metal oxide thin films.
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1. Introduction

Thin films of vanadium dioxide have been the subject of intensive research efforts in recent years due to their potential application as "smart" window coating [1,2] and various other advanced technological applications such as infrared modulators [3] or in data storage [4,5]. All of these technologies are based on the thermochromic metal to semiconductor transition that occurs in pure single crystals of vanadium dioxide at 68 °C. This transition is associated with a structural phase change from a low temperature monoclinic phase (VO_2 M) to a higher temperature rutile phase (VO_2 R) [6]. This phase change leads to significant changes in optical properties and electrical conductivity. The higher temperature rutile material is metallic and reflects infra-red solar radiation, whereas the monoclinic phase, is a semiconductor and generally transmissive to all solar radiation.

Significant challenges exist that need to be addressed before thermochromic technology can be widely employed. Principally the phase transition temperature. At 68 °C this is too high for practical application in "smart" glazing. The ideal transition temperature is likely to depend on the climate the glazing is used in; it is expected to be in the range 20 – 30 °C [7].

The introduction of dopants has been demonstrated to affect the thermochromic transition temperature [8]. It has been observed that high valence metal ions, such as W^{6+} or Nb^{5+}, when doped into vanadium dioxide, decrease the metal to semiconductor (MST) temperature of vanadium dioxide. Low valence ions, such as Al^{3+} or Cr^{3+} have been shown to increase the MST temperature [9]. It has been observed that dopant ions with an ionic radius smaller than V^{4+}, or that created V^{5+} defects (which were smaller than V^{4+}) increased the MST temperature, while dopant ions with a larger ionic radius than V^{4+} caused a decrease in the MST temperature [10].

Tungsten has been shown to be the most effective of the dopants investigated so far [11–15], it has been found to reduce the transition temperature of vanadium dioxide by the greatest extent per atom % and as such is the dopant that the focus of the majority of research has been on [9,12,16–24]. For all reported methods of preparation, vanadium dioxide films containing ~2 atm % tungsten have been shown to have a thermochromic transition temperature of about 25 °C, however, these reports also suggest that tungsten doping has a deleterious effect on the transition, reducing the change in IR reflectance [23].

Other work on the effect of film thickness has also been conducted and indicates a reduction in film thickness also leads to a reduction in transition temperature [25–27]. However, subsequent studies suggested that the reduction in transition temperature is likely to be a result of an increase in stress in the film [28], which can be caused by crystallographic orientation [12]. Further recent studies have also suggested that plasmonic effects resulting from reduced crystallite sizes can also significantly reduce the transition temperature [29].

It is this focus on control of particle size that concerns us here. Previous studies have shown that the application of electric fields to chemical vapour deposition reactions is capable of reducing the

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Table 1
Table indicating electric field strength, deposition temperature and compositional information. All films were grown from the aerosol chemical vapour deposition of a 0.1 M solution of [VO(acac)$_2$] in ethanol onto gas sensor or glass substrates.

Sample	Deposition temperature (°C)	Applied potential difference (Vm^{-1}) [type]	Substrate	Material phase determined by XRD/RAMAN/WDAX
A	450	15 [DC]	Gas sensor	VO_2 (m) + VO_2 (B)
B	525	15 [AC]	Gas sensor	VO_2 (m),
C	525	15 [DC]	Gas sensor	VO_2 (m),
D	600	15 [DC]	Gas sensor	VO_2 (m), V_2O_5
E	600	15 [AC]	Gas sensor	VO_2 (m), V_2O_5
F	525	0	Glass	VO_2 (m),
G	525	15 [AC]	Glass	VO_2 (m),

particle size of the deposited material substantially [30–32]. In this paper we report on further work in this area utilizing a wider range of parameters.

2. Experimental details

2.1. Film synthesis

Films were deposited using electric field-assisted chemical vapour deposition (EACVD) onto gas sensor and glass substrates. The experimental setup, procedure for deposition onto glass substrates [32] and the building of gas sensor substrates [30] has been previously described in detail. The precursor used for the depositions was vanadyl acetylacetonate [VO(acac)$_2$] (Aldrich 99.9%). For each deposition, standard solutions of 20 mL of 0.1 M in ethanol were used.

An aerosol was created using a Vicks ultrasonic humidifier and the mist was observed before the reaction was initiated by the addition of the carrier gas, which was N_2 (BOC, 99.99%). In all cases, the carrier gas flow rate was 1 $Lmin^{-1}$ and a substrate temperature of 450–600 °C was used. In the case of gas sensor substrates the substrate temperature was controlled by incorporation of the platinum heater track (on the base of the sensor substrate) into a Wheatstone bridge circuit. In the case of glass substrates heating was achieved using a graphite block with an embedded heater cartridge. All depositions were carried out for a period of between 10 and 30 min. An electric field was created by applying a specific potential difference across the electrodes of the gas sensor substrate or between the transparent conducting oxide layers of top and bottom glass substrates. Both DC and AC biases (the latter associated to a frequency of 50 Hz) were used and the applied voltage kept constant at 15 V.

2.2. Materials characterization

Scanning electron microscopy (SEM) was conducted using a JEOL-6301 F field emission Scanning Microscope operated with an accelerating voltage of 5 kV. Raman spectroscopy was carried out using a Renishaw inVia Raman (Renishaw Raman System 1000) microscope using a green argon ion laser of wavelength 514.5 nm. X ray diffraction (XRD) was carried out using a micro focus Bruker Discover D8 diffractometer with a wide-angle Gadds detector using $CuK_{\alpha 1+2}$ radiation (λ = 1.546 Å) in reflection mode using a glancing incident angle of 5°. X-ray photoelectron spectroscopy, (XPS) was performed on a Kratos Axis Ultra-DLD photoelectron spectrometer using monochromatic Al-Kα radiation. Survey spectra were collected at a pass energy of 160 eV, whilst narrow scans acquired at a pass energy of 40 eV, charge neutralization of the samples was achieved using the Kratos immersion lens neutralization system. The data was analyzed using CasaXPS software and calibrated to the C(1 s) signal at 284.1 eV, attributed to adventitious carbon. Atomic force microscopy (AFM) was used to evaluate roughness of the films and was conducted using a Dimension 3100 instrument in tapping mode. Water contact angle measurements were carried out using a Goniometer Kruss DSA100 drop shape analyzer. Optical properties were evaluated using a Perkin Elmer Lambda 950 instrument with a variable temperature stage.

3. Results and discussion

The EACVD reaction of vanadyl acetylacetonate in ethanol onto a glass or gas sensor substrates afforded yellow/brown films. A summary of growth conditions and compositional analysis is presented in Table 1. The films were highly adherent to the substrate passing the Scotch tape test, they could not be wiped off with a piece of toweling and resisted scratching with a brass stylus, however, they could be abraded with a steel stylus.

EDAX spot analysis confirmed the presence of vanadium and oxygen in the films and indicated that no other element was present, at least to the limit of detection (~0.5 at.%). Scanning electron microscopy of the films (Fig. 1.) indicated that the application of electric fields to the reaction and change in deposition temperature had a profound effect on the morphology of the deposited films.

For the samples deposited on gas sensor substrates (Fig. 1.), deposition temperature was found to have a profound effect on the film morphology. Films deposited at 450 °C (Fig. 1A.) consisted of spherical island growths between 500 and 750 nm in diameter, similar in shape but somewhat larger than those produced from previous work [33], this is attributed to an increase in growth rate as a consequence of the application of an electric field [30]. Higher temperatures (525 °C, Fig. 1B & C.) lead to the production of films with ill-defined shrub like morphologies that appear extremely porous with a fine structure with a scale length in the 10's of nm's. This is in marked contrast to films produced under identical conditions but without the application of an electric field [30]. The morphology for these samples was broadly similar irrespective of the type of electric field applied. Increasing the deposition temperature further still (600 °C) led to the production of films with nanowire systems branching in a pseudo dendritic like fashion (Fig. 1D & E). The nanowires were found to have a diameter between 5 and 10 nm.

X-ray diffraction of the EACVD samples (Fig. 2.) showed significant peak broadening compared with films made from AACVD alone [30–32] the majority phase was found to be monoclinic vanadium dioxide (JCPDS file number 43–1051), although the broadening of the peaks may obscure peaks from other phases such as V_2O_5. For this reason we tentatively evaluate crystallite size [34] from the X-ray diffraction data as an average crystallite size of less than 10 nm. The strength of the applied field made little difference to the observed X-ray diffraction pattern. In all cases where an electric field was applied during the deposition reaction substantial peak broadening is observed. For samples D and E, which were deposited at 600 °C, additional peaks relating to V_2O_5 are observed, undoubtedly due to surface oxidation and the proportionately higher surface to bulk ratio that is apparent from the nanowire nature of these samples.

XPS of the film surface (not shown) indicated multiple vanadium and oxygen environments for all of the samples examined. Modeled 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 [35]. The O 1 s peak is centered at 530.9 eV and is quite broad and asymmetric, indicating more than one oxygen environment is present, consistent with multiple vanadium oxide environments. Previous work has reported the presence of fully oxidized vanadium at the surface [36], as such the observation of multiple vanadium environments is not surprising.

Raman spectroscopy (Fig. 3.) of the EACVD samples indicated that only significant stretches to VO_2 were present although some minor stretches relating to V_2O_5 could be discerned, similar to previous work conducted with EACVD [30–32]. Raman spectroscopy also confirmed the presence of graphitic carbon with two large, broad peaks centered on 1100 and 1400 cm^{-1} [30–32].

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