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Templated growth of smart coatings: Hybrid chemical vapour deposition of vanadyl acetylacetonate with tetraoctyl ammonium bromide

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ABSTRACT

Hybrid aerosol assisted and atmospheric pressure chemical vapour deposition methodology has been utilised to produce thin films of vanadium dioxide from vanadyl acetylacetonate. Tetraoctyl ammonium bromide (TOAB) was used in the aerosol precursor solution. The films were analysed by X-ray diffraction, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy. Their optical and thermochromic behaviour was also determined. It was found that the use of TOAB had a templating effect that led to a halving in the particle size and that this consequently led to a significant decrease in the thermochromic transition temperature of the films to 34 °C.

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1. Introduction

Vanadium dioxide is a material that has shown potential for use as an intelligent glazing material [1,2]. The material has a metal to semiconductor transition (MST) where there is a structural change from a higher temperature rutile structure to a lower temperature monoclinic structure [3]. This structural transition results in a change in electrical conductivity and optical properties. The rutile material is metallic and reflects a wide range of solar radiation; whereas the monoclinic phase is a semiconductor and generally transparent to solar radiation.

The temperature this phase change occurs as is 68 °C in single crystal vanadium dioxide [3], it is considered that in order for vanadium dioxide to be a useful material in intelligent glazing this transition temperature needs to be reduced to around 25 °C [4]. Work has been conducted in recent years to try and reduce the transition temperature of the vanadium dioxide MST by adding dopants [5,6], of which tungsten has been the most successful dopant; reducing the MST by 20–25 °C per at.% of tungsten dopant [7].

There are however a variety of problems with adding dopants to the films. Results on the effect of tungsten and fluorine dopants show that fluorine doping increased the transmission of the metallic state thus diminishing the overall level of switch and subsequent efficiency of the film [8]. The same effect is seen in the case of tungsten doping where the transmission of the semiconducting state is reduced also lowering the overall switch [9].

In order to have as large a switch as possible the transition temperature must be reduced in an alternative manner. It has been demonstrated that by adding strain into a VO_2 film the transition temperature may also be reduced. This may be done by substrate matching [10], using sub 50 nm thin films (in physical vapour deposition processes) [11] or by introducing preferential orientation through the careful choice of chemical vapour deposition (CVD) growth conditions [12].

Surfactant templates have been used in CVD previously to control the size of deposited gold nanoparticles in both aerosol assisted CVD (AACVD) and the hybrid system [13–15]. In each case, the surfactant is added to the precursor solution and mixed before use. In other examples a template is printed onto the substrate prior to deposition [16] or the surface is saturated by gaseous exposure before the main deposition process begins [17].

A hybrid chemical vapour deposition methodology has previously been used to deposit thin films of gold nanoparticle doped vanadium dioxide from the chemical vapour deposition reaction of vanadyl acetylacetonate and auric acid in methanol [15]. This hybrid technique shows great potential as the film characteristics are similar to those produced by atmospheric pressure chemical vapour deposition (APCVD – good adhesion, uniformity and coverage) but with the precursor versatility afforded by AACVD. Here we report on depositions carried out using this hybrid methodology, vanadyl acetylacetonate and the

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surfactant molecule, tetraoctyl ammonium bromide (TOAB), to directly influence film growth. It was found that the use of TOAB in the hybrid reaction lead to template affects where the VO_2 crystallite size was reduced; subsequently adding strain into the films and significantly reducing the metal semi-conductor transition temperature.

2. Experimental

A 98% nitrogen, 2% oxygen mixture was obtained from the British Oxygen Company (BOC) and used as supplied in the plain line. Nitrogen (99.99%) was obtained from BOC and used as supplied in the bubbler lines. Coatings were obtained on SiO_2 coated float glass. Combined AA/AP CVD experiments were conducted on 150 mm × 45 mm × 3 mm pieces of glass using a flat-bed cold-walled CVD reactor. The glass was cleaned prior to use by washing with petroleum ether (60–80 °C) and isopropanol and then dried in air. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt–Rh thermocouple. Independent thermocouple measurements indicated that temperature gradients of up to 50 °C cm^{-1} were observable at 600 °C across the surface of the glass. The rig was designed so that four independent gas lines could be used. All gas handling lines, regulators and flow valves were made of stainless steel and were 6.5 mm internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus that were 13 mm in diameter. In these experiments three gas lines were used. Gases came directly from a cylinder and were preheated by passing along 2 m lengths of stainless steel tubing, which were curled and inserted inside a tube furnace. The temperatures of all the gas inlet lines were monitored by Pt–Rh thermocouples and Eurotherm heat controllers.

Vanadyl acetylacetonate (99.99%) – $[VO(acac)_2]$ – was obtained from Aldrich and used without further purification and was placed into a stainless steel bubbler. The bubbler was heated to 175 °C by a heating jacket and vanadyl acetylacetonate introduced into the gas streams by passing hot nitrogen gas through the bubbler. Tetraoctyl ammonium bromide was obtained from Aldrich and used without further purification. In deposition experiments using TOAB, between 1 g and 0.1 g was added to the reaction flask and stirred for 10 min prior to the deposition experiment. An aerosol was generated at room temperature by use of a PIFCO air humidifier. Nitrogen was passed through the aerosol mist, thus forcing the aerosol particles encapsulated with precursor into the heated reaction chamber.

The two components of the system were transported using stainless steel pipes 13 mm internal diameter respectively. The pipes were attached directly to the reaction chamber of the coater. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. This deposition set up has been described in more detail previously [15]. All of the apparatus was baked out with nitrogen at 150 °C for 30 min before use. Deposition experiments were conducted by heating the horizontal-bed reactor and the bubblers to the desired temperatures before diverting the nitrogen line through the bubbler and hence to the reactor. Deposition experiments were timed by use of a stopwatch and were conducted for typically 15 min. The maximum possible deposition temperature with this equipment was 600 °C. At the end of the deposition only nitrogen was allowed to flow over the glass substrate until the substrate had sufficiently cooled to handle (~60 °C). Samples were handled and stored in air. Substrate temperature for deposition was kept constant at 525 °C as this has been found to be the optimal temperature to grow monoclinic vanadium dioxide thin films from vanadyl acetylacetonate. Due to the nature of the graphite heating block there are subtle changes in thickness that correlate with the temperature gradient across the substrate however, a highly uniform area 2 cm × 5 cm in the middle of the substrate is always observed, it is this area that is referred to when discussing the uniformity of the films.

Electron microprobe analysis was obtained on a JEOL EMA and referenced against vanadium and oxygen standards. Energy dispersive analysis of X-rays (EDAX) and wavelength dispersive analysis of X-rays (WDAX) 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 (XRD) patterns were measured on a Bruker Gadds D8 diffractometer using monochromated ($CuK_{\alpha 1+2}$) radiation in the reflection mode using a glancing incident angle of 5°. X-ray photoelectron spectra were recorded with a VG ESCALAB 220I XL instrument using a focused (300 μm spot) monochromatic AlK_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.6 eV. Depth profiling measurements were obtained by using argon beam sputtering. Reflectance and transmission spectra were recorded between 300 nm and 2500 nm on a PerkinElmer Lambda 950 UV–vis spectrometer. UV–vis spectra were obtained using a Helios double beam instrument. 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. Transmittance-temperature studies (transition temperature and hysteresis width measurements) were performed on a PerkinElmer 457 grating spectrometer set to 4000 cm^{-1}. An aluminium temperature cell controlled by RS resistive heaters, Eurotherm temperature controllers and k-type thermocouples was used to manipulate sample temperature. Sample temperature was measured using a k-type thermocouple taped directly onto the film surface. Film thickness was measured directly by scanning electron microscopy then correlated with EDAX and optical transmission data.

3. Results

VO_2 films were grown by the use of hybrid aerosol assisted atmospheric pressure CVD from TOAB in methanol and $[VO(acac)_2]$. The films showed good surface coverage, uniformity and reproducibility. Film thickness could be easily varied by increasing or decreasing the time of deposition. In all cases at least the first 75% of the substrate is covered, similar to that observed previously with VO_2 films produced from the APCVD

Table 1
Summary of experimental conditions and chemical analysis. Flow conditions and deposition time were constant for all experiments; plain flow = 2 L min^{-1}, $VO(acac)_2$ bubbler flow = 4 L min^{-1}, aerosol flow = 1 L min^{-1} and deposition time 15 min; content of AACVD flask: 25 ml of methanol with variable amount of TOAB as shown in the table.

Sample	TOAB amount (g)	EDAX/WDAX/XRD phase	λ_{max} in visible transmission (film colour) (nm)
1	Not used	VO_2 (monoclinic)	569
2	1.00	VO_2 (monoclinic)	568
3	0.50	VO_2 (monoclinic)	566
4	0.25	VO_2 (monoclinic)	570
5	0.12	VO_2 (monoclinic)	566
6	0.06	VO_2 (monoclinic)	567

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