JOURNAL OF Materials CHEMISTRY

Atmospheric pressure chemical vapour deposition of vanadium(V) oxide films on glass substrates from reactions of $VOCl_3$ and VCl_4 with water

M. N. Field and I. P. Parkin*

Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ

Received 16th March 2000, Accepted 16th May 2000
Published on the Web 23rd June 2000

Reaction of VCl_4 or $VOCl_3$ with water under atmospheric pressure chemical vapour deposition conditions in a cold-wall horizontal-bed reactor at 350–600 °C produces clear yellow V_2O_5 films. Films grown at temperatures in excess of 500 °C were crystalline and indexed with an orthorhombic unit cell $a = 11.527(5)$, $b = 4.382(5)$, $c = 3.557(5)$ Å by glancing angle X-ray diffraction (XRD). X-Ray photoelectron spectroscopy (XPS) showed the presence of carbon, vanadium and oxygen in the surface layer. Depth profile sputtering removed the carbon and left only vanadium and oxygen with binding energies of 516.0 eV for V $2p_{3/2}$ and 530.5 eV for O 1s. The vanadium to oxygen ratio, as determined by XPS, was 1 : 2, indicating some preferential loss of oxygen during sputtering. Raman spectroscopy of the films showed identical patterns to bulk and magnetron sputtered V_2O_5 with bands at 697, 524, 478, 401, 300, 283, 194, 145 and 103 cm^{-1}. All films passed the Scotch tape test and could not be abraded with a paper towel or scratched with a scalpel. The visible and near IR reflectance spectra of the films show that they are more reflective than plain glass in the IR region. Transmission spectra of the films showed that they have equivalent transmission to plain glass but have a transmission cut off that is shifted 110 nm into the visible. The conditions established are attractive for the large scale rapid production of vanadium(V) oxide films.

Introduction

Vanadium oxide thin films have been looked at for a number of reasons. Many of these oxides are shown to undergo thermochromic phase transitions such as at 257 °C for V_2O_5[1] and at 68 °C for VO_2.[2] These switching characteristics have led to them being proposed for use in optical switching and storage devices. V_2O_5 has also been shown to have electrochromic properties, being able to change from blue to green to yellow with a response time of *ca.* 2 seconds.[3] Other uses for vanadium oxide films include solid-state lithium-ion batteries and the window in solar cells and gas detectors.[4] Deposition of vanadium oxide thin films has been complicated by the fact that vanadium has a wide variety of stable oxidation states and that formation of solid solutions with different stoichiometry is relatively easy. This has meant that the exact deposition and sputtering conditions, with attention to precursor, oxidizing conditions and reactor design, have proved determinant in obtaining single phase films. Despite this, V_2O_5 films have been made in many ways including the sol–gel technique,[5] sputtering using a vanadium source in an oxygen atmosphere,[6] vacuum evaporation,[7] as well as low pressure chemical vapour deposition (LPCVD) from $VO(OC_2H_5)_3$ precursors.[8] V_2O_5 films have also been grown at atmospheric pressure from the vapour transport reaction of $VOCl_3$ and carbon dioxide at 127 °C[10] and the reaction of $VO(OC_3H_7)_3$ in a moving conveyor belt CVD process at 600 °C.[11] In the latter case the films were a mixture of V_2O_5 and VO_2.

We have an interest in forming thin films of metal oxides, nitrides and sulfides on glass substrates by atmospheric pressure chemical vapour deposition (APCVD) using readily available starting materials.[9] APCVD has the advantages of using relatively simple apparatus (no vacuum system required), exceptionally fast growth rates and good conformal coverage of the whole substrate. Previously we have investigated the formation of chromium oxide films from the reaction of water and CrO_2Cl_2 and the formation of titanium oxide films from $TiCl_4$ and water.[9] Unfortunately in both cases the films were hazy, patchy and particulate. Substantial pre-reaction occurred in the mixing chamber before the coater leading to blockages in the gas delivery lines. Improvements in the formation of chromium oxide and titanium dioxide coatings was achieved by replacing water with other oxygen sources such as methanol and ethanol.[9] However these sources did incorporate some carbon into the films. It was also concluded from these studies that water is too reactive to be a useful oxygen source for uniform coatings, as it reacts in the gas phase within the mixing chamber to form gas-phase particulates that consequently give rise to poor films.

Here, we report on the reactions of VCl_4 and $VOCl_3$ with water under APCVD conditions to produce optically transparent, adhesive, conformal, yellow films of single phase V_2O_5. Notably no problems of pre-reaction or formation of particulate films were observed in these systems.

Experimental

The substrate for the APCVD experiments consisted of SiCO undercoated glass 225 mm × 90 mm × 4 mm in dimension. The glass was cleaned prior to use by rinsing with petroleum spirit (bp 40–60 °C) and propan-2-ol then air-dried. VCl_4 and $VOCl_3$ (both 99%+, purchased from Aldrich Chemical Co.) were used as the vanadium sources. Distilled water was used as the oxygen source for the reactions.

The APCVD experiments were carried out in a purpose built apparatus, consisting of a horizontal-bed, cold-wall reactor connected by an arrangement of 6 mm diameter heated stainless steel pipes and valves, through which nitrogen carrier gas (99.99%; BOC) and precursors were passed (Fig. 1). All

This journal is © The Royal Society of Chemistry 2000

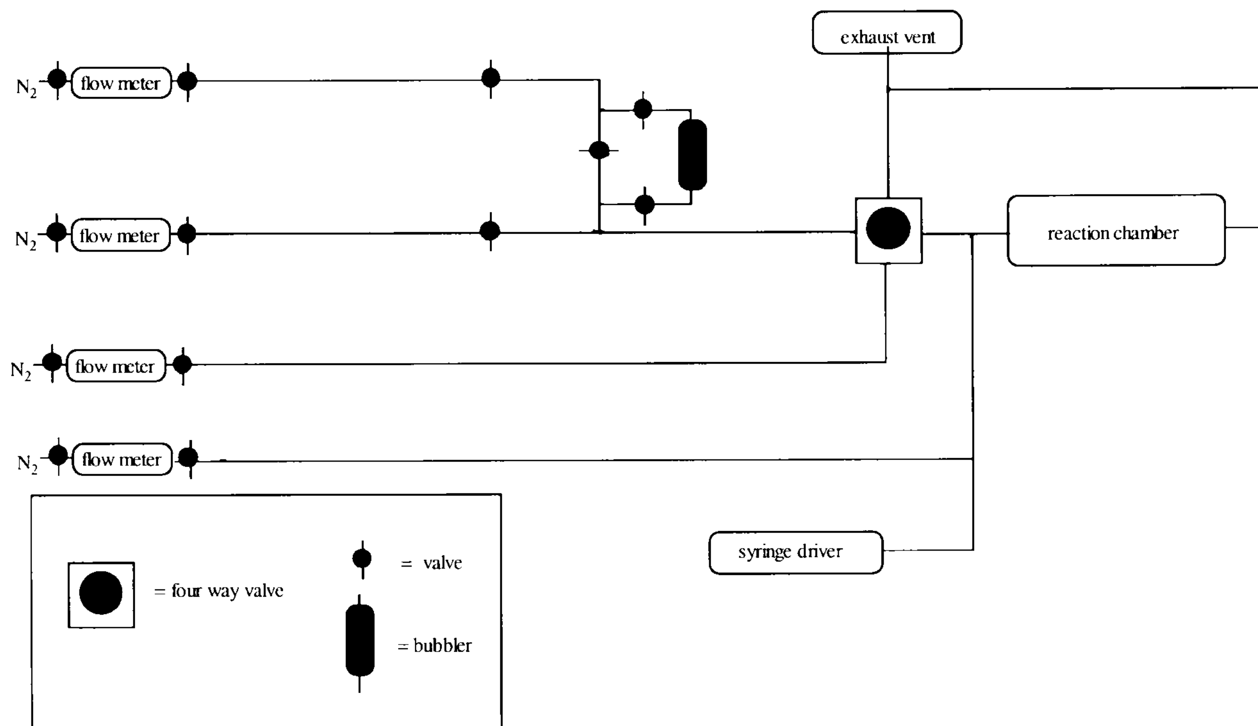


Fig. 1 Schematic line diagram showing the pipework arrangement used in the APCVD experiments.

pipework was heated by electrical tape. The temperatures of the various parts of the rig were monitored and controlled by Eurotherm controllers. The apparatus was flushed with nitrogen for 30 min before and after each deposition. Nitrogen was used without drying and flow-levels in the reactor were monitored by gauges. The total gas flow-rate through the reactor was 12.6 $dm^3 min^{-1}$ during deposition experiments and 2 $dm^3 min^{-1}$ during the heating and cooling stages. The exhaust gases leave the reactor *via* a 13 mm internal diameter stainless steel pipe.

All reactions were carried out at atmospheric pressure. The vanadium precursors were introduced into the gas phase by passing nitrogen gas through a bubbler containing the heated precursor. The vanadium precursor bubbler was set at 90 °C for the $VOCl_3$ experiments and at 100 °C for the VCl_4 experiments. The flow of nitrogen carrier gas through the bubbler was set at either 333 or 666 $cm^3 min^{-1}$. A co-reactant oxygen source was introduced by injecting water into a nitrogen carrier gas stream (150 °C, 2 $dm^3 min^{-1}$) at a rate of 1.33 $cm^3 min^{-1}$. The nitrogen-diluted vanadium and water–nitrogen streams were mixed by means of two concentric pipes. The inner pipe contained the vanadium precursor vapour and the outer pipe the co-reactant water vapour. The inner pipe was three centimetres shorter than the outer pipe. This allowed mixing of the precursor streams prior to entering the coater. The reactor hot-zone consisted of a carbon block which was heated by three Whatman cartridge heaters. CVD experiments were conducted from 300–600 °C (at 50 °C intervals) for between 30–180 s for each system. A variation of *ca.* 10 °C was noted between the edge and the centre of the substrate during the APCVD experiments. The glass substrate was allowed to cool with the graphite block to *ca.* 60 °C before it was removed.

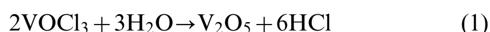
Coated substrates were handled and stored in air. The large coated glass sample was broken up into *ca.* 1 cm × 1 cm squares for subsequent analysis by XPS, EDAX, SEM, electron probe and optical studies. Large pieces of glass (*ca.* 4 cm × 4 cm) were used for X-ray powder diffraction, Raman and Scotch tape tests.

X-Ray powder diffraction patterns were measured on a Philips X-pert diffractometer using nickel-filtered Cu-Kα_1 ($\lambda = 1.5045$ Å) radiation in the reflection mode using a glancing incident angle. Samples were optimised using Unit Cell[12] and compared to database standards. SEM/EDAX was obtained on a Hitachi S570 instrument using the KEVEX system. Growth rates were shown to be *ca.* 300 nm min^{-1}, for the films deposited at a substrate temperature of 500 °C. X-Ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focussed (300 nm spot) monochromatic Al-Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 20 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 profile measurements were obtained by using argon beam sputtering. UV–Vis spectra were recorded in the range 190–800 nm using a Shimadzu double-beam instrument, band gaps were calculated by the direct method. Transmission–reflection spectra were measured on a purpose built machine utilising two Zeiss miniature monolithic spectrometers connected to a PC. Raman spectra were acquired using an Olympus BH-2 microscope coupled to either a Dilor XY triple grating spectrometer or a Renishaw Raman system 1000. The Dilor system used an excitation line wavelength 632.8 nm from a Coherent Innova 300 Kr^+ laser. The Renishaw systems were calibrated against the emission lines of neon.

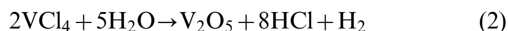
Results

Reaction of $VOCl_3$ and water under APCVD conditions at substrate temperatures from 350–600 °C produced V_2O_5 coatings. Reactions of VCl_4 and water under similar conditions did not produce a film at substrate temperatures below 450 °C. With both vanadium precursors no reaction took place in the absence of water even at the highest deposition temperature of 600 °C. The films produced were a transparent yellow colour and formed a uniform film over the whole substrate with no evidence of particulate growth. All films adhered firmly to the glass substrate and passed the Scotch tape and scalpel-scratch tests. The films showed no change upon storage in air at room temperature for over two years. Idealised

equations for the reactions are shown in eqn. (1) and (2).



$$2VOCl_3 + 3H_2O \rightarrow V_2O_5 + 6HCl \quad (1)$$



$$2VCl_4 + 5H_2O \rightarrow V_2O_5 + 8HCl + H_2 \quad (2)$$

Film characterisation

The XPS analysis of the thin films showed that only vanadium, oxygen and some carbon were present on the surface layer of the films. Notably, no chlorine was detected in any of the films by XPS. On XPS depth-profiling using argon ion etching, the carbon content was removed to trace levels and only vanadium and oxygen were observed (Fig. 2). The XPS binding energy shifts for vanadium $2p_{3/2}$ were 516.0(1) eV for all of the films, this compares to 516.2 eV for magnetron sputtered V_2O_5 and 516.5 eV for bulk V_2O_5.[13] The oxygen binding energy was 530.5 eV, consistent with the formation of O^{2-}. Transition metal oxides have reported binding energies in the range 529.5–531.3 eV.[13]

XPS depth profile analysis showed that after Ar^+ ion etching a V to O ratio of 1 : 2 was observed for films produced from both $VOCl_3$ and VCl_4 with water. This is lower than that expected for V_2O_5 films and may be due to the preferential removal of oxygen during the etching of the sample. This is a common phenomenon in the XPS analysis of thin films.[13]

Raman spectroscopy (Fig. 3) showed that the product formed from the reactions of both $VOCl_3$ and VCl_4 with water was V_2O_5, as the peak positions (at 697, 524, 478, 401, 300, 283, 194, 145 and 103 cm^{-1}) and intensities agreed exactly with previous literature measurements for V_2O_5.[14]

The X-ray diffraction patterns of the films grown from VCl_4 or $VOCl_3$ with water gave diffuse diffraction peaks. For the films grown at the highest temperatures (550–600 °C) the patterns were of sufficient quality to be indexed. These all showed an orthorhombic unit cell. The lattice parameters for the film grown at 550 °C from $VOCl_3$ and water were $a = 11.527(5)$, $b = 4.382(5)$ $c = 3.557(5)$ Å. The other crystalline films indexed within 0.01 Å of these parameters. This indexing agrees well for that of bulk semiconducting V_2O_5, $a = 11.519(3)$, $b = 4.373(3)$ $c = 3.564(5)$ Å.[15] No preferred orientation was observed in the V_2O_5 films.

The scanning electron micrographs (SEM) of the films produced from the reaction of $VOCl_3$ and VCl_4 with water showed that the films consisted of randomly shaped overlapping island-growths approximately 100 nm across. The morphology of the film was independent of the substrate deposition temperature. The growth pattern is typical for that expected of the Volmer–Webber type.[9] SEM measurements gave a film thickness of 700–1000 nm for films grown over a 3 minute period at 500 °C. Consistent with a growth rate of *ca.* 300 nm min^{-1}. Energy dispersive X-ray analysis showed that

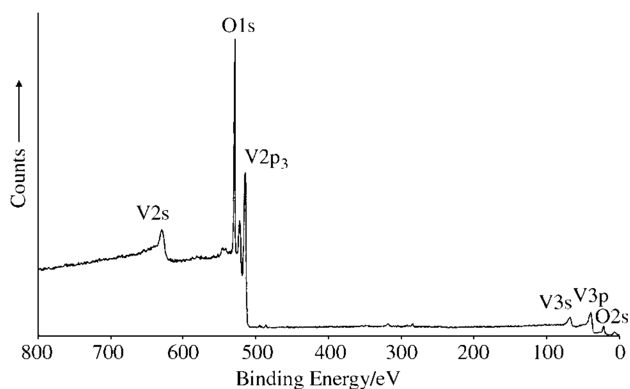


Fig. 2 X-Ray photoelectron spectrum of the film prepared from the APCVD reaction of $VOCl_3$ and water at 550 °C after 20 minutes of Ar^+ depth profiling.

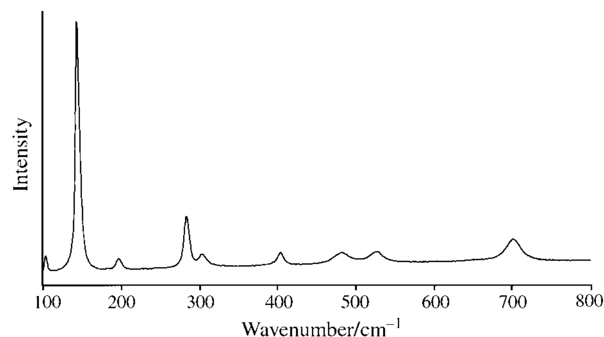


Fig. 3 Raman spectrum for the V_2O_5 film prepared from the APCVD reaction of $VOCl_3$ and water at 550 °C.

the films contained only vanadium (oxygen was below the instrument cut-off) and no chlorine. The excitation volume in the EDX system used had a depth of 1 μm and consequently did show breakthrough excitations from the underlying glass.

The optical transmission properties of the V_2O_5 coated glass were very similar to those of plain glass, however the transmission cut off is shifted 110 nm into the visible region (Fig. 4a and 4b). The V_2O_5 coated glass showed improved reflectivity in the IR region compared to plain glass. The transmission properties of magnetron sputtered V_2O_5 has been extensively investigated. The APCVD prepared films match previous studies.[11] The calculated optical band gaps for the 3 minute runs of both $VOCl_3$ and VCl_4 were 2.47–2.53 eV. This compares exactly with magnetron sputtered V_2O_5 and is close to bulk V_2O_5 at 2.45 eV.[16,17]

Discussion

It was found that $VOCl_3$ would react with water under APCVD conditions at significantly lower temperatures than VCl_4. This could be due to the $VOCl_3$ already containing a VO bond. Vanadium pentoxide films made using either precursor displayed equivalent physical properties.

The as-formed films were yellow and were identical in colour to bulk single crystals of pure V_2O_5. Notably, introduction of

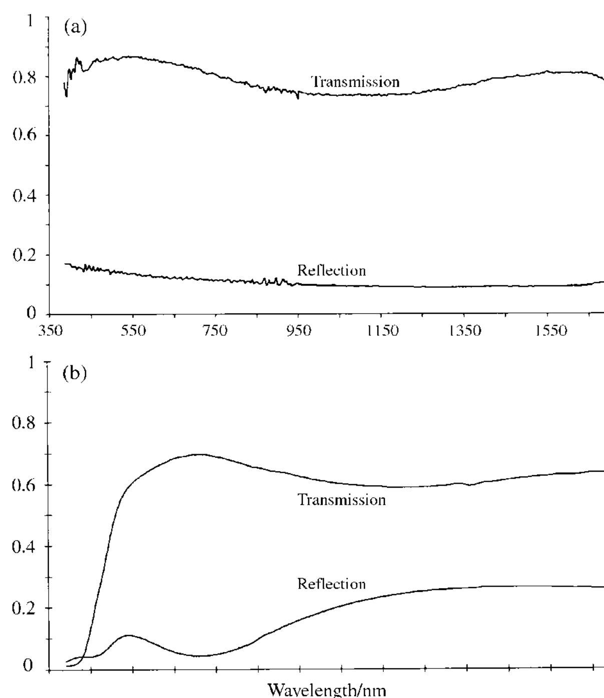


Fig. 4 Reflectance and transmission plots against wavelength for: (a) plain glass and (b) a V_2O_5 film prepared from the APCVD reaction of $VOCl_3$ and water at 550 °C.

trace amounts of impurities into bulk or thin film V_2O_5 and/or partial reduction of the vanadium gives rise to green coloured materials. Hence, purely on the basis of colour, the V_2O_5 films produced in this study were comparable to fully stochiometric V_2O_5. All of the physical analysis techniques were also in agreement with the formation of fully stoichiometric V_2O_5 with the exception of the XPS study, which indicated from analysis of the peak areas formation of VO_2. This is most likely due to preferential sputtering of oxygen during depth profiling.

The use of VCl_4 as a precursor to form vanadium pentoxide films means that the vanadium has been oxidised in the reaction. It is possible that under APCVD conditions water is acting as the oxidising agent, although it cannot be ruled out that some trace oxygen in the system or from the glass plays a role. Another interesting feature is that chlorine is not incorporated in the films. In low pressure CVD, and CVD of metal and electronic substrates, the use of chlorine based precursors can cause substrate etching. Furthermore, as the process is invariably at low temperature, chlorine contamination can be a problem. Under APCVD conditions at temperatures in excess of 350 °C on glass substrates we have not observed any incorporation of chlorine in the films, either in this study or our previous work.[9]

In reactions with vanadium halides and oxyhalides, water can be used as an oxygen source, unlike our previous comparable studies of reacting water with $TiCl_4$ and CrO_2Cl_2, where particulate, poorly adherent, hazy films of TiO_2 and Cr_2O_3 were produced.[9] Essentially the same apparatus, flow rates and reaction conditions were employed in both experiments. The fact that good films could be obtained from the vanadium system is probably a consequence of a slower reaction rate in the gas phase at the mixing chamber temperatures of *ca.* 200 °C.

Conclusions

V_2O_5 films can be prepared by atmospheric pressure CVD techniques using relatively inexpensive and readily available starting materials. The V_2O_5 films were yellow, fully stoichiometric, uniform, transparent and adhesive to the substrate. The APCVD reactions use readily available starting materials and offer easy access to high quality films.

Acknowledgements

I. P. P. and M. F. thank the EPSRC for a studentship and for grant GR/M98623. I. P. P. thanks the Royal Society for provision of a Carl Zeiss miniature spectrometer. Prof. R. J. H. Clark and Miss A. M. E. Hardy are thanked for assistance with Raman measurements.

References

1 G. S. Nadkarni and V. S. Shirodkar, *Thin Solid Films*, 1983, **105**, 115.
2 J. F. De Natale, P. J. Hood and A. B. Harker, *J. Appl. Phys.*, 1989, **66**, 5844.
3 Y. Shimizu, K. Nagase, N. Mirura and N. Yamazoe, *Solid State Ionics*, 1992, **53–56**, 490.
4 Y. Sato, T. Nomura, H. Tanaka and K. Kobayakawa, *J. Electrochem. Soc.*, 1991, **138**, L37.
5 V. Vivier, J. Farcy and J. P. Pereira-Ramos, *Electrochim. Acta*, 1998, **44**, 831.
6 A. Cricenti, M. Girasole, R. Generosi, C. Coluzza, S. Capone and P. Siciliano, *Appl. Phys. A: Mater. Sci. Proc.*, 1998, **66**, S1175.
7 Z. S. Guan, J. N. Yao, Y. A. Yang and B. H. Loo, *J. Electoanal. Chem.*, 1998, **443**, 175.
8 T. Maruyama and Y. Ikuta, *J. Mater. Sci.*, 1993, **28**, 5073.
9 L. S. Price, I. P. Parkin, T. G. Hibbert and K. C. Molloy, *Chem. Vap. Deposition*, 1998, **4**, 222; L. S. Price, I. P. Parkin, A. Hardy, R. J. H. Clark, T. G. Hibbert and K. C. Molloy, *Chem. Mater.*, 1999, **11**, 1792; I. P. Parkin and M. N. Field, *J. Phys. IV*, 1999, **9**, 387; I. P. Parkin and G. E. Elwin, *Chem. Vap. Deposition*, 2000, **6**, 59.
10 J. B. MacChesney, J. F. Potter and H. J. Guggenheim, *J. Electrochem. Soc.*, 1968, **115**, 52.
11 J. B. Greenberg, *Thin Solid Films*, 1983, **110**, 73.
12 T. J. B. Holland and S. A. T. Redfern, Unit Cell, Department of Earth Sciences, Cambridge University, 1995.
13 C. D. Wagner, in *Practical Surface Analysis*, 2nd edn, ed. D. Briggs and M. Peah, Wiley, Chichester, 1990, **vol. 1**.
14 N. Ozer and C. Cronin, *Thin Solid Films*, 1995, **265**, 28.
15 R. Enjalbert and J. Galy, *Acta Crystallogr., Sect. C*, 1986, **42**, 1497.
16 C. R. Aita, Y. L. Liu, M. L. Kao and S. D. Hansen, *J. Appl. Phys.*, 1986, **60**, 749.
17 M. Ghanashyam Krishna, Y. Debauge and A. K. Bhattacharya, *Thin Solid Films*, 1998, **312**, 116.