



Atmospheric pressure chemical vapour deposition of vanadium arsenide thin films via the reaction of VCl_4 or VOCl_3 with ${}^1\text{BuAsH}_2$ ☆

Tegan Thomas, Christopher S. Blackman, Ivan P. Parkin, Claire J. Carmalt*

Materials Chemistry Centre, Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

ARTICLE INFO

Article history:

Received 6 September 2012
Received in revised form 25 April 2013
Accepted 26 April 2013
Available online 7 May 2013

Keywords:

Arsenide
Chemical vapour deposition
Thin film

ABSTRACT

Thin films of vanadium arsenide were deposited via the dual-source atmospheric pressure chemical vapour deposition reactions of VCl_4 or VOCl_3 with ${}^1\text{BuAsH}_2$. Using the vanadium precursor VCl_4 , films were deposited at substrate temperatures of 550–600 °C, which were black-gold in appearance and were found to be metal-rich with high levels of chlorine incorporation. The use of VOCl_3 as the vanadium source resulted in films being deposited between 450 and 600 °C and, unlike when using VCl_4 , were silver in appearance. The films deposited using VOCl_3 demonstrated vanadium to arsenic ratios close to 1:1, and negligible chlorine incorporation. Films deposited using either vanadium precursor were identified as VAs using powder X-ray diffraction and possessed borderline metallic/semiconductor resistivities.

© 2013 The authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

Bulk transition metal arsenides exhibit a range of potentially industrially important properties including negative electrode materials for Li-ion batteries [1] and superconductors [2]. Although bulk transition metal arsenides have been well studied [3–5], knowledge regarding transition metal arsenide thin films remains limited although related nitride [6–11] and phosphide [12–16] films have been reported, most likely due to the availability of suitable volatile precursors. However, due to recent advances in precursor technology, research into this area has been facilitated.

Both single- and dual-source routes have been used in the deposition of transition metal arsenide thin films [17]. Single-source precursors such as $[\text{Co}_2(\text{CO})_6\text{As}_2]$ and $[\text{Co}(\text{CO})_2\{\text{As}^t\text{Bu}_2\text{H}\}(\text{NO})]$ have been used to deposit CoAs thin films, with consistent films also deposited via a dual-source route using tricarbonylnitrosylcobalt and di-tertiarybutyl arsine [18]. Other attempts to deposit SnAs and TiAs films using single-source precursors resulted in the deposition of SnO_2 and TiO_2 films respectively [19,20]. However, recently, the dual-source atmospheric pressure chemical vapour deposition (APCVD) reactions of TiCl_4 and ${}^1\text{BuAsH}_2$ [21], and $[\text{Ti}(\text{NMe}_2)_4]$ and ${}^1\text{BuAsH}_2$ [22] have been reported and resulted in the deposition of TiAs thin films. Films obtained via both routes were highly crystalline with borderline metallic/semiconductor resistivities.

Following the deposition of TiAs films via dual-source APCVD, it was hoped that a similar methodology could be used to deposit VAs

films. Dual-source APCVD routes to VP films have already been reported for the APCVD reactions of VCl_4 , VOCl_3 or $[\text{V}(\text{NMe}_2)_4]$ with $\text{C}_y\text{H}_{\text{hex}}\text{PH}_2$ [23,24] and additionally VOCl_3 with $\text{P}(\text{SiMe}_3)_3$ [23]. In light of the use of the arsenic precursor, ${}^1\text{BuAsH}_2$, in the deposition of TiAs films, and the vanadium precursors VCl_4 and VOCl_3 for the formation of VP films, herein we describe the APCVD reactions of VCl_4 and VOCl_3 with ${}^1\text{BuAsH}_2$ resulting in the deposition of VAs films.

2. Experimental details

2.1. Precursors and substrate

Vanadium (IV) chloride (99.9%, Acros Organic), VOCl_3 (99.9%, Alfa Aesar), and ${}^1\text{BuAsH}_2$ (SAFC Hitech Ltd.), were all utilised in APCVD via containment within stainless steel bubblers. Both the VCl_4 and VOCl_3 bubblers were fitted with heating jackets set to 100 °C and 55 °C in all instances, resulting in vapour pressures of approximately 13.3 kPa and 9.3 kPa, respectively. Due to the high volatility of ${}^1\text{BuAsH}_2$ a heating jacket was not required, with ${}^1\text{BuAsH}_2$ being used in all instances at room temperature, resulting in an approximate vapour pressure of 24.0 kPa. All reagents were used as supplied, without further purification.

Depositions were conducted on 90 mm × 45 mm × 4 mm SiCO float-glass supplied by Pilkington NSG, with substrates cleaned using petroleum ether (60–80 °C) and 2-propanol, and allowed to air dry prior to use.

Caution: The use of ${}^1\text{BuAsH}_2$ could potentially produce highly toxic AsH_3 during the CVD reaction. All experiments were conducted in a fume cupboard, with the gas from the CVD process treated with a bleach bubbler to destroy any potential AsH_3 present.

☆ This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

* Corresponding author. Tel.: +44 207 6797528; fax: +44 207 6797463.

E-mail address: c.j.carmalt@ucl.ac.uk (C.J. Carmalt).

2.2. APCVD equipment and methods

All APCVD experiments were conducted using a horizontal-bed cold-wall quartz reactor, comprising of a graphite heating block containing a Watlow cartridge heater, with temperature control achieved using Pt–Rh thermocouples. The equipment, parameters and methodology are identical to those previously reported [25].

The APCVD reactions of VCl_4 and VOCl_3 with ${}^t\text{BuAsH}_2$ were investigated using substrate temperatures of 450–600 °C and deposition time lengths of either 60 or 120 s. Whilst the APCVD using the vanadium precursor VCl_4 was only conducted using a 1:2 ratio of VCl_4 to ${}^t\text{BuAsH}_2$, reactions using VOCl_3 were investigated using 1:2, 1:4 and 1:6 ratios of VOCl_3 to ${}^t\text{BuAsH}_2$ to determine how a change in ratio affected the deposited films. Exact experimental parameters for the APCVD reactions are described in Table 1.

Following deposition completion, the CVD chamber and substrate were allowed to cool to room temperature under a flow of nitrogen. The substrate plus deposit was then extracted and stored in air.

2.3. Film analysis

Scanning electron microscopy (SEM) analysis was conducted using a JSM-6301F scanning field emission machine with an operating voltage of 5 keV. X-ray powder diffraction (XRD) patterns were obtained using monochromatic $\text{Cu-K}\alpha$ radiation on a Brüker AXS D8 discover machine. Wavelength dispersive X-ray (WDX) analysis was conducted using a Philips XL30ESEM machine. X-ray photoelectron spectroscopy (XPS) was performed at the University of Nottingham using a Kratos Axis Ultra DLD spectrometer, using a monochromated $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) X-ray source. The photoelectrons were detected using a hemispherical analyser with channel plates and Delay line detector. The binding energies were referenced to an adventitious C 1s 40 peak at 284.9 eV. Raman spectra were acquired using 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. Reflectance and transmittance spectra were recorded between 300 and 1200 nm using a Perkin Elmer lambda 950 photospectrometer. Measurements were standardised relative to a spectralab standard mirror (reflectance) and air (transmittance). Water contact angle measurements were conducted by measuring the spread of an 8 μl drop of water, and applying an appropriate calculation.

3. Results and discussion

3.1. Film deposition and visual appearance

The APCVD reaction of VCl_4 and ${}^t\text{BuAsH}_2$ resulted in the deposition of black-gold films on glass between substrate temperatures of 550–600 °C (Table 1). The deposited films exhibited limited coverage ($\sim 1\text{--}2$ cm²) and were restricted to the hottest part of the glass

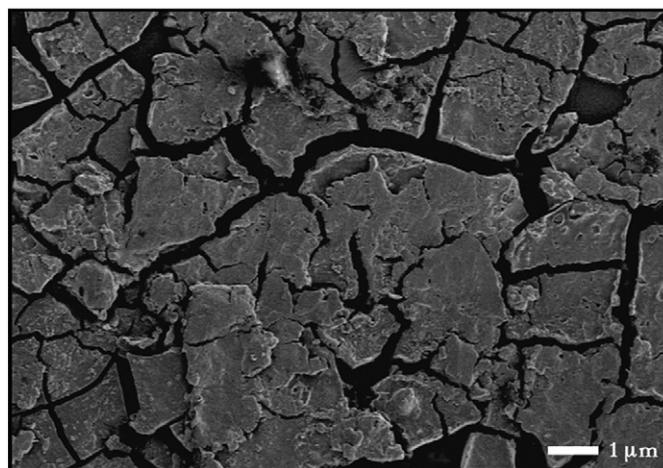


Fig. 1. Scanning electron micrograph of the film deposited via the APCVD of VCl_4 and ${}^t\text{BuAsH}_2$ at 600 °C using a deposition time of 120 s showing the fractured surface ($\times 1000$ magnification).

substrate (centre of the substrate) which is approximately 25 °C hotter than at the substrate edge. The appearance and limited deposition of the films was found to be consistent with VP films deposited via the APCVD of VCl_4 or VOCl_3 with $\text{Cy}^{\text{Hex}}\text{PH}_2$, and additionally VP films deposited via the APCVD of VOCl_3 with $\text{P}(\text{SiMe}_3)_3$ [23].

In contrast to films deposited using VCl_4 , when using the vanadium precursor VOCl_3 , film deposition was observed for substrate temperatures between 450 and 600 °C. Films deposited at temperatures lower than 450 °C were however poor in quality, and as such, only films deposited at substrate temperatures of 550 and 600 °C were investigated in detail. In contrast to the black-gold films deposited from VCl_4 , VOCl_3 produced films which were silver in appearance and highly reflective. These films were consistent in appearance to VP films deposited via the APCVD of $[\text{V}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{Hex}}\text{PH}_2$ [24].

Side-on scanning electron microscopy (SEM) was used to determine film thickness and hence approximate deposition rates for the films. A deposition rate of ~ 100 nm min^{-1} was calculated for APCVD depositions of $\text{VCl}_4/{}^t\text{BuAsH}_2$ and ~ 50 nm min^{-1} when using $\text{VOCl}_3/{}^t\text{BuAsH}_2$. This observed decrease in deposition rate on changing from VCl_4 to VOCl_3 is consistent with that obtained for the APCVD deposition of VP using VCl_4 or VOCl_3 and $\text{Cy}^{\text{Hex}}\text{PH}_2$ [23].

SEM was also used to determine the morphology of the deposited films. A fractured film surface was observed from the SEM of the film formed from VCl_4 and ${}^t\text{BuAsH}_2$ at 600 °C, which consisted of roughly spherical agglomerates approximately 100 nm in size (Fig. 1). In contrast, all films deposited using VOCl_3 and ${}^t\text{BuAsH}_2$, exhibited continuous material deposit, with good substrate coverage (Fig. 2). However, the films also consisted of roughly spherical agglomerates approximately 100 nm in size, consistent with an island growth mechanism, as seen with previously deposited TiAs films [21,22].

Table 1

Experimental conditions used to deposit films via the APCVD of vanadium precursor (VCl_4 or VOCl_3) and ${}^t\text{BuAsH}_2$.

| | Film | Substrate temp, °C | N_2 flow rate through vanadium precursor bubbler, L/min (mol/min) | N_2 flow rate through ${}^t\text{BuAsH}_2$ bubbler, L/min; (mol/min) | Plain line flow, L/min; Mixing chamber temp, °C | Deposition time, secs |
|-----------------|------|--------------------|--|---|---|-----------------------|
| VCl_4 | 1 | 550 | 0.1; (0.000621) | 0.1; (0.00128) | 4; 130 | 60 |
| | 2 | 550 | 0.1; (0.000621) | 0.1; (0.00128) | 4; 130 | 120 |
| | 3 | 600 | 0.1; (0.000621) | 0.1; (0.00128) | 4; 130 | 60 |
| | 4 | 600 | 0.1; (0.000621) | 0.1; (0.00128) | 4; 135 | 120 |
| VOCl_3 | 5 | 550 | 0.15; (0.000614) | 0.2; (0.00257) | 4; 125 | 60 |
| | 6 | 550 | 0.15; (0.000614) | 0.3; (0.00385) | 4; 130 | 60 |
| | 7 | 550 | 0.15; (0.000614) | 0.1; (0.00128) | 4; 125 | 120 |
| | 8 | 550 | 0.15; (0.000614) | 0.2; (0.00257) | 4; 130 | 120 |
| | 9 | 600 | 0.15; (0.000614) | 0.2; (0.00257) | 4; 130 | 60 |

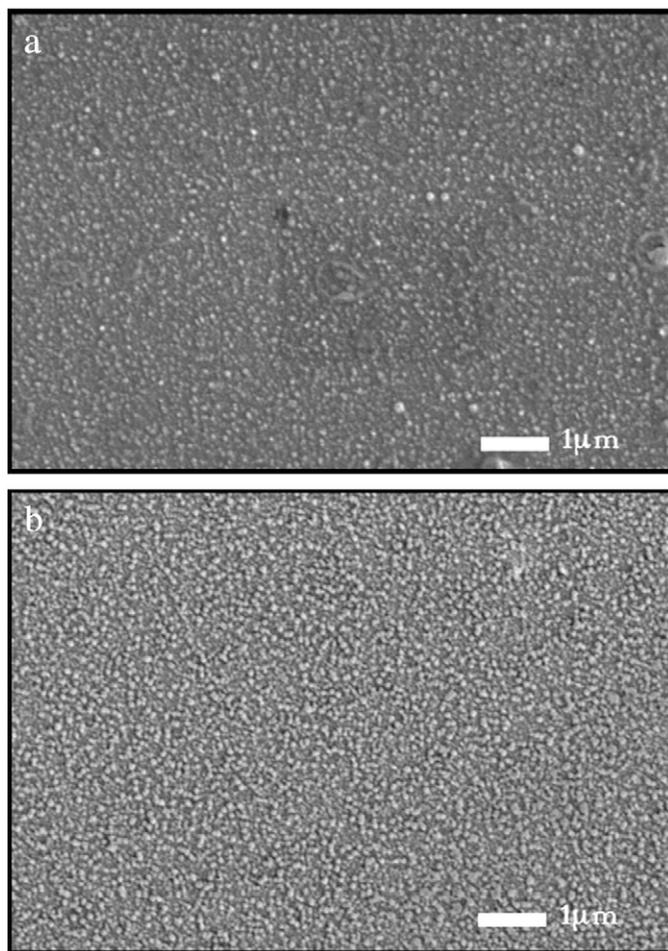


Fig. 2. Scanning electron micrographs of films deposited via the APCVD of VOCl_3 and ${}^1\text{BuAsH}_2$ at 550 °C using a VOCl_3 to ${}^1\text{BuAsH}_2$ ratio of 1:4 and deposition times of 60 (a) and 120 s (b) ($\times 10,000$ magnification).

3.2. Film characterisation

The X-ray powder diffraction of films deposited using either VCl_4 or VOCl_3 as vanadium precursors produced consistent diffractograms (Fig. 3). Peaks were observed at approximately 32.6, 34.2, 41.2, 42.5, 46.0, 49.1, 50.2, 51.6, 55.0, and 56.7 $2\theta^\circ$ consistent with the formation of VAs [26]. In addition to these peaks, a broad peak at approximately 22° and a peak at approximately 38.8° were also observed in the diffractograms. The peak at 22° was attributed to the underlying

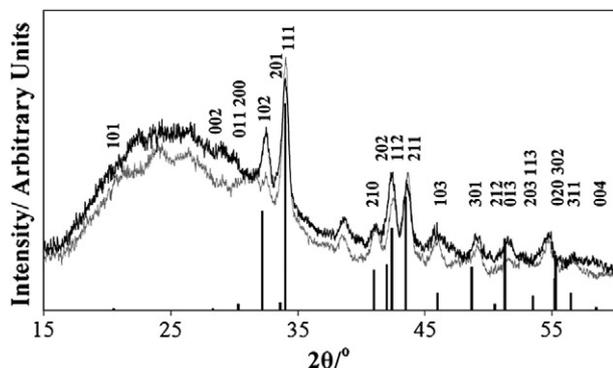


Fig. 3. Typical X-ray powder diffraction patterns for films deposited via the APCVD of VCl_4 (black) and VOCl_3 (grey) with ${}^1\text{BuAsH}_2$ with comparison to a reference VAs diffractogram of bulk material.

glass substrate, however due to the lack of other associated peaks, the peak at 38.8° could not be attributed to a particular species, however it was likely to be due to a vanadium or arsenic oxide species.

In order to determine and compare the elemental compositions of the films, wavelength dispersive X-ray (WDX) analysis was employed (Fig. 4). All films deposited using VCl_4 were found to be vanadium rich and demonstrated variable elemental ratios depending on the specific deposition conditions. On comparing films deposited using VCl_4 at the same substrate temperature but different deposition time length (film 1 vs. 2, and 3 vs. 4) large differences between the vanadium to arsenic ratios were observed, which is likely due to the relative thickness of the VO_x layer due to film oxidation. Additionally, although chlorine incorporation was found to be negligible in VP films deposited via the APCVD of VCl_4 and $\text{Cy}^{\text{Hex}}\text{PH}_2$ [23], films deposited here using VCl_4 and ${}^1\text{BuAsH}_2$ exhibited high levels of chlorine incorporation (approximately 5–11 atm.%). Although this was inconsistent with previously reported VP films, this relatively high level of chlorine incorporation was comparable with that previously reported for the deposition of TiAs films via the APCVD of TiCl_4 and ${}^1\text{BuAsH}_2$ [21]. Films deposited using VOCl_3 were found to be slightly arsenic rich with vanadium to arsenic ratios close to 1:1 (Fig. 4). In contrast to films deposited using VCl_4 , the films demonstrated negligible chlorine incorporation, consistent with that previously reported for VP films deposited using VOCl_3 and $\text{Cy}^{\text{Hex}}\text{PH}_2$ [23].

X-ray photoelectron spectroscopy (XPS) was conducted on film 4 (film deposited using the vanadium precursor VCl_4) and film 7 (film grown using VOCl_3). For film 4, after etching through the surface layer three vanadium environments were detected at 516.5, 515.3 and 513.9 eV. The peak at 516.5 eV is consistent with literature values for V_2O_5 (~517 eV) [27,28]. The peak at 513.9 eV was found to be comparable to that previously attributed to VP [23,24] and the peak at 515.3 eV was assigned to a vanadium arsenate [21], however as there is an overlap of the As 3d ionisation peaks with that of V 3d peaks, assignment of corresponding As 3d_{5/2} was not possible. Two major O 2p ionisations were observed at 530.3 and 532.1 eV, being consistent with that expected for V_2O_5 , and SiO_2 , respectively. Additionally, a small Cl 1s ionisation peak was observed at 199.7 eV, which is consistent with the observation of Cl incorporation from WDX analysis. Similarly for film 7, three vanadium environments were detected at 514.4, 515.6 and 516.5 eV assigned to vanadium arsenide, vanadium arsenate and V_2O_5 , respectively. Overall, 75% vanadium species was bound to arsenic in a roughly 1:2 ratio of arsenide to arsenate with 25% of the film being V_2O_5 at/near the surface. This is comparable to previous reports on TiAs thin films, which also

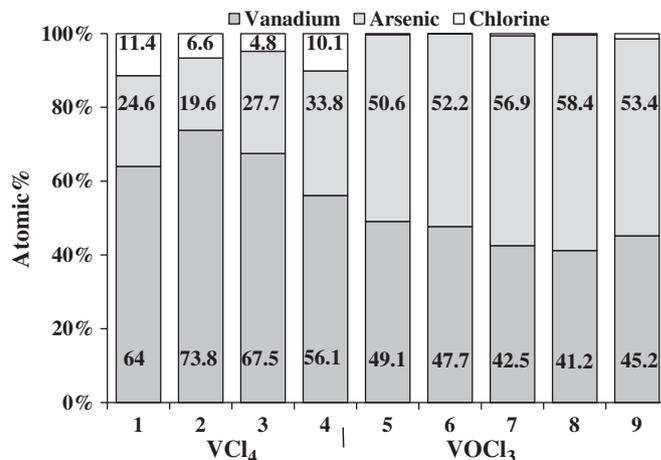


Fig. 4. Schematic representation of atomic percentage compositions for films deposited via the APCVD of VCl_4 and VOCl_3 with ${}^1\text{BuAsH}_2$.

showed peaks due to titanium arsenide, titanium arsenate and titanium oxide [21].

In comparison to film 4, film 7 (film deposited via the APCVD of VOCl_3 to ${}^1\text{BuAsH}_2$) demonstrated similar V $2p_{3/2}$ ionisation environments at 516.5, 515.2 and 514.4 eV, which were attributed to V_2O_5 [27], V_2O_3 [28] and VAs [23,24], respectively. In addition, the O $2p$ ionisation had two major peaks at 530.2 and 532.0 eV, again consistent with the presence of V_2O_5 or V_2O_3 , and SiO_2 respectively. Unlike when using the vanadium precursor VCl_4 , a barely detectable Cl $1s$ was observed, supporting the WDX results of the film, which indicated negligible chlorine incorporation.

Raman microscopy was conducted on films deposited via both the APCVD of VCl_4 and VOCl_3 with ${}^1\text{BuAsH}_2$. For films deposited using the vanadium precursor VCl_4 two distinct Raman patterns were observed. When using VCl_4 and a deposition time of 60 s films exhibited intense broad peaks at approximately 499 and 680 cm^{-1} , which is consistent with the formation of V_2O_5 [29]. However, when using VCl_4 with a deposition time of 120 s these characteristic vanadium oxides peaks were not observed. Instead, the films exhibited broad peaks at approximately 226, 933 and 988 cm^{-1} , which could be attributed to the formation of VAs. However, the Raman spectra for VAs have not been reported previously and are presented in Fig. 5 for these films.

Unlike that observed for films deposited using the vanadium precursor VCl_4 , no films deposited using VOCl_3 produced Raman patterns consistent with the formation of V_2O_5 . All patterns were found to be consistent with that observed for films deposited using VCl_4 with deposition times of 120 s, and again were attributed to VAs (Fig. 5).

3.3. Film properties

All obtained films, regardless of which vanadium precursor was used, demonstrated good substrate adherence. All films passed the Scotch-tape test, with the film deposited at 600 °C for 60 s using VOCl_3 (film 9) being the only film to pass the steel stylus test, thereby demonstrating a film hardness greater than that previously reported for VP [23], and of a similar hardness to TiAs [21]. All films demonstrated borderline metallic/semiconductor-like conductivities, with resistivities in the range of 200–400 $\mu\Omega\cdot\text{cm}$, similar to that previously reported for both VP [24] and TiAs [21,22].

All tested films exhibited decreased reflectivity within the IR region, with a slight increase in reflectivity within the UV (~400 nm). No difference in reflectivities was observed for films deposited using the same conditions but different precursor ratios, however it was noted that on comparing films 5 and 8 (deposition temperature of 550 °C, $\text{VOCl}_3: {}^1\text{BuAsH}_2 = \sim 1:4$, and deposition times of 60 and 120 s respectively) an increase in reflectivity was observed for the film deposited for 60 s (film 5), as shown in Fig. 6. As mentioned

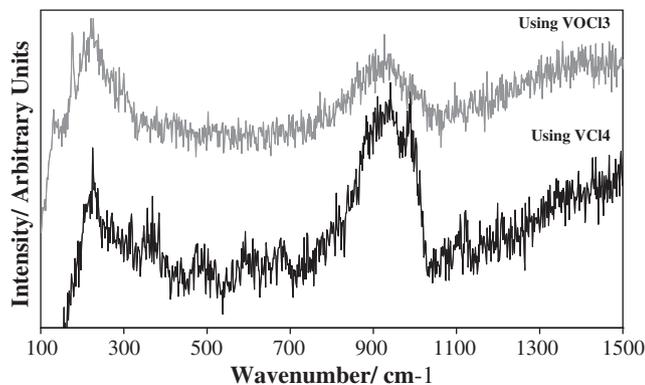


Fig. 5. Comparison of typical Raman spectra for VAs films deposited via the APCVD of VOCl_3 and ${}^1\text{BuAsH}_2$ and VCl_4 and ${}^1\text{BuAsH}_2$.

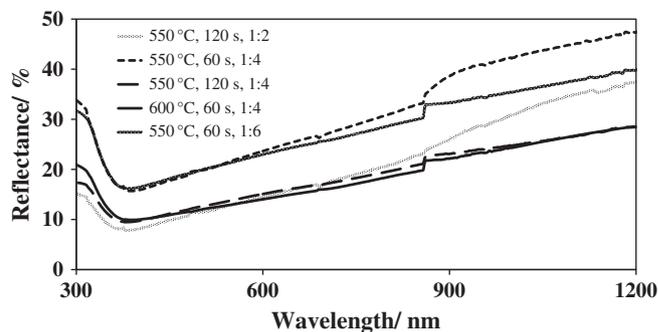


Fig. 6. Reflectance data for VAs films deposited via the APCVD of VOCl_3 and ${}^1\text{BuAsH}_2$ using a range of substrate temperatures, deposition times, and VOCl_3 to ${}^1\text{BuAsH}_2$ ratios.

previously, WDX results indicated that the vanadium to arsenic ratio in film 5 was closer to 1:1, and as such, the higher reflectance observed in film 5 was considered to be a truer property of VAs films. VAs films deposited using VOCl_3 were found to exhibit lower transmittance over the range of 1200–300 nm than that reported when using VCl_4 , this is indicative of the thicker films deposited when using VOCl_3 .

Water contact angles between 30 and 45° were observed for films deposited using VCl_4 at 550 °C (films 1 and 2), with these low contact angles thought to be due to the high levels of film oxidation. Similarly, for films deposited using VCl_4 at 600 °C (films 3 and 4), smaller contact angles (25–75°) were observed for the films deposited for 120 s (film 4) compared to that deposited for 60 s (85–95° for film 3); this again was attributed to higher degrees of oxidation in film 4. Films deposited using VOCl_3 displayed higher contact angles (40–75°) than those reported when using VCl_4 , which was due to the low levels of film oxidation when using VOCl_3 , and consistent with those previously reported for TiAs films [21,22].

4. Discussion

The results described above show that the vanadium precursor used had a significant effect on the stoichiometry and quality of the films produced. The APCVD experiments show that using VCl_4 as the vanadium precursor led to vanadium-rich VAs films probably due to the co-formation of a vanadium oxide under some conditions with significant contamination by chlorine. Powder XRD indicated that the films were VAs, however, compositional analysis revealed the presence of contaminants (Cl) and non-stoichiometric nature of the films. Vanadium oxychloride (VOCl_3) was found to be a much better precursor for the APCVD of vanadium arsenide thin films. The films produced from VOCl_3 and ${}^1\text{BuAsH}_2$ had an arsenic to vanadium ratio close to 1 and negligible contamination from chlorine. Powder XRD and Raman analysis were consistent with the formation of VAs and the films had a silver appearance. These results can be compared to previous APCVD work on vanadium phosphide where limited film growth could be produced using VCl_4 (and $\text{Cy}^{\text{hex}}\text{PH}_2$), whereas VP thin films were produced using VOCl_3 [23]. These vanadium phosphide films were similar in appearance to the arsenide films, described herein from VCl_4 and ${}^1\text{BuAsH}_2$. In contrast, and somewhat surprisingly, the films deposited from VOCl_3 and ${}^1\text{BuAsH}_2$ were more consistent in appearance (silver) to higher quality VP films deposited via the APCVD of $[\text{V}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ [24]. The high level of chlorine incorporation in the $\text{VCl}_4/{}^1\text{BuAsH}_2$ films is comparable with that previously reported for the deposition of TiAs films via the APCVD of TiCl_4 and ${}^1\text{BuAsH}_2$ [21].

We have previously used VOCl_3 as a precursor in CVD, primarily for the formation of vanadium oxide [29] and oxynitride [30] films at temperatures below 650 °C. Higher temperatures (above 800 °C)

are typically required when using VOCl_3 to fully eliminate oxygen and produce pure films, such as vanadium nitride [31] or vanadium borides [32]. However, we have shown here that VOCl_3 is an effective precursor and APCVD is a good method for forming VAs films.

5. Conclusions

VAs films have been deposited via the APCVD reactions of both VCl_4 and VOCl_3 with ${}^1\text{BuAsH}_2$. Crystalline VAs films were deposited via the APCVD of VCl_4 and ${}^1\text{BuAsH}_2$ at substrate temperatures of 550–600 °C. The films were black-gold in appearance, and demonstrated limited substrate coverage, which was consistent with that reported for VP films. The films were found to be metal-rich, with high levels of chlorine incorporation, and demonstrated borderline metallic/semiconductor resistivities.

Films deposited when using the vanadium precursor VOCl_3 were silver in appearance, and were deposited between the substrate temperatures of 450–600 °C. The films demonstrated good substrate coverage, were typically slightly arsenic-rich with a V:As ratio close to 1 and contained negligible chlorine incorporation. Similarly to when using VCl_4 , the films exhibited borderline metallic/semiconductor resistivities, consistent with previously reported TiAs films.

All films were VAs from powder X-ray diffraction, with extra peaks believed to be due to the presence of vanadium oxide species. Reflectance, transmittance and water contact angles of the films were consistent with those previously reported for TiAs.

Acknowledgements

The EPSRC is thanked for a studentship (TT). Pilkington NSG are thanked for providing the glass substrates. SAFC Hitech Ltd. is thanked for the supply of ${}^1\text{BuAsH}_2$. Dr Emily Smith (University of Nottingham) is thanked for carrying out XPS analysis under EPSRC grant EP/F019750/1: “A Coordinated Open-Access Centre for Comprehensive Materials Analysis”.

References

- [1] M.P. Bichat, F. Gillot, L. Monconduit, F. Favier, M. Morcrette, F. Lemoigno, M. Doublet, *Chem. Mater.* 16 (2004) 1002.
- [2] D.G. Hinks, *Nat. Phys.* 5 (2009) 386.
- [3] A.L. Hector, I.P. Parkin, *Z. Naturforsch Teil B. Chem.* 49 (1994) 477.
- [4] A.L. Hector, I.P. Parkin, *J. Mater. Chem.* 4 (1994) 279.
- [5] I.P. Parkin, *Chem. Soc. Rev.* 25 (1996) 199.
- [6] R. Fix, R.G. Gordon, D.M. Hoffman, *Chem. Mater.* 3 (1991) 1138.
- [7] R.M. Fix, R.G. Gordon, D.M. Hoffman, *Chem. Mater.* 2 (1990) 235.
- [8] A.C. Newport, C.J. Carmalt, I.P. Parkin, S.A. O'Neill, *Eur. J. Inorg. Chem.* (2004) 4286.
- [9] S.R. Kurtz, R.G. Gordon, *Thin Solid Films* 140 (1986) 277.
- [10] J.P. Dekker, P.J. Vanderput, H.J. Veringa, J. Schoonman, *J. Electrochem. Soc.* 141 (1994) 787.
- [11] A.C. Newport, J.E. Bleau, C.J. Carmalt, I.P. Parkin, S.A. O'Neill, *J. Mater. Chem.* 14 (2004) 3333.
- [12] C. Blackman, C.J. Carmalt, S.A. O'Neill, I.P. Parkin, L. Apostolico, K.C. Molloy, *J. Mater. Chem.* 11 (2001) 2408.
- [13] C.S. Blackman, C.J. Carmalt, S.A. O'Neill, I.P. Parkin, L. Apostolico, K.C. Molloy, *Chem. Mater.* 16 (2004) 1120.
- [14] C.S. Blackman, C.J. Carmalt, I.P. Parkin, S.A. O'Neill, K.C. Molloy, L. Apostolico, *Mater. Lett.* 57 (2003) 2634.
- [15] C.S. Blackman, C.J. Carmalt, T.D. Manning, I.P. Parkin, L. Apostolico, K.C. Molloy, *Appl. Surf. Sci.* 233 (2004) 24.
- [16] C.S. Blackman, C.J. Carmalt, T.D. Manning, S.A. O'Neill, I.P. Parkin, L. Apostolico, K.C. Molloy, *Chem. Vap. Depos.* 9 (2003) 10.
- [17] F.R. Klingan, A. Miehr, R.A. Fischer, W.A. Herrmann, *Appl. Phys. Lett.* 67 (1995) 822.
- [18] Y. Senzaki, W.L. Gladfelter, *Polyhedron* 13 (1994) 1159.
- [19] M.F. Mahon, N.L. Moldovan, K.C. Molloy, A. Muresan, I. Silaghi-Dumitrescu, L. Silaghi-Dumitrescu, *Dalton Trans.* (2004) 4017.
- [20] T. Thomas, D. Pugh, I.P. Parkin, C.J. Carmalt, *Dalton Trans.* 39 (2010) 5325.
- [21] T. Thomas, C.S. Blackman, I.P. Parkin, C.J. Carmalt, *Eur. J. Inorg. Chem.* (2010) 5629.
- [22] T. Thomas, C.S. Blackman, I.P. Parkin, C.J. Carmalt, *Dalton Trans.* 40 (2011) 10664.
- [23] C.S. Blackman, C.J. Carmalt, S.A. O'Neill, I.P. Parkin, K.C. Molloy, L. Apostolico, *J. Mater. Chem.* 13 (2003) 1930.
- [24] C.S. Blackman, C.J. Carmalt, S.A. O'Neill, I.P. Parkin, K.C. Molloy, L. Apostolico, *Chem. Vap. Depos.* 10 (2004) 253.
- [25] C. Blackman, C.J. Carmalt, I.P. Parkin, S. O'Neill, L. Apostolico, K.C. Molloy, S. Rushworth, *Chem. Mater.* 14 (2002) 3167.
- [26] K. Bachmayer, H.N. Nowotny, *Monatsh. Chem.* 86 (1955) 741.
- [27] J. Soria, J.C. Conesa, M.L. Granados, R. Mariscal, J.L.G. Fierro, J.F.G. Delabanda, H. Heinemann, *J. Catal.* 120 (1989) 457.
- [28] B. Horvath, J. Strutz, J. Geyerlippmann, E.G. Horvath, *Z. Anorg. Allg. Chem.* 483 (1981) 181.
- [29] C. Piccirillo, R. Binions, I.P. Parkin, *Chem. Vap. Depos.* 13 (2007) 145.
- [30] T.D. Manning, I.P. Parkin, R.J.H. Clark, D. Sheel, M.E. Pemble, D. Vernadou, *J. Mater. Chem.* 12 (2002) 2936; M.N. Field, I.P. Parkin, *J. Mater. Chem.* 10 (2000) 1863.
- [31] A. Leonhardt, M. Seidler, E. Wolf, M. Schoenherr, A. Zetsche, H. Mai, *Ger.(East)*, CODEN:GEXXA8, DD288628, 1991. 3.
- [32] H. Mikami, C.J. Zhou, S. Takahashi, T. Sato, K. Shimakage, *Shigen Sozai* 110 (1994) 313.