Formation of VN from VCl_4 and $NH(SiMe_3)_2$ by APCVD − a Potential Solar Control Coating

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Vanadium nitride thin films have been synthesised by the reaction of vanadium(IV) chloride with hexamethyldisilazane (HMDS) under atmospheric pressure (AP)CVD conditions at 300–550 °C. The films deposited have good optical characteristics and low electrical resistivities. These films were not scratched off the glass substrate by a steel stylus and were not degraded by immersion in a range of solvents. X-ray diffraction showed an NaCl-type cubic cell with a = 4.102(1)–4.127(1) Å, dependent on the sample. X-ray photoelectron spectroscopy shows that the films have a V/N ratio close to unity. For comparison, films were also deposited by the APCVD reaction of $VOCl_3$ with HMDS. These films consist of mixed phases of vanadium oxynitride and V_2O_3. The VN films show properties suitable for use as solar control coatings.

Introduction

Vanadium nitride is a hard refractory material with metallic properties.[1] In its purest form it has a gold colour. Like the other transition metal nitrides it has many uses especially when deposited as a thin film.[2,3] Vanadium nitride has good metallic conductivity and stability to heat that makes it suitable as a barrier coating for microelectronic devices.[4] It is resistant to chemical attack by most solvents and reagents apart from hydrofluoric acid and aqua regia. The mechanical hardness of VN films has found application in wear-resistant parts.

Vanadium nitride films have been deposited under atmospheric pressure chemical vapour deposition (APCVD) conditions by reaction of vanadium chloride with nitrogen/hydrogen or ammonia[5] and reactions of vanadium amides $\{[V(NR_2)_4]; R = Me, Et\}$.[6] The former method evolved hydrogen chloride gas that is undesirable in the synthesis of films for microelectronic devices due to its corrosive nature.[5] The latter method yielded polycrystalline films with pinhole defects as result of rapid gas phase nucleation. This method also produced organic by-products.[7,8] Other methods of producing VN thin films include: N_2/H_2 plasma processing,[9] ion beam assisted deposition,[10] magnetron sputtering,[11] molecular organic CVD,[12] and pulsed laser deposition.[13]

Single-source CVD methods to prepare VN have also been reported using $[V(NR)Cl_3]$ (R = Me, C_6H_4Me, tBu).[14] Unfortunately, the use of single-source precursors have so far yielded films with significant carbon contamination.[14] The presence of carbon can affect the optical properties of the film, whereas low amounts of oxygen seemingly do not.[15] It should be noted that in the case of VN, films have been classified as vanadium nitride with over 40 atom% carbon and oxygen contents. The decomposition of $[V(N\textit{t}Bu)Cl_3]$ gave films at temperatures as low as 250 °C that were shown to be vanadium carbonitride upon analysis.[14] Related precursors, $[V(NMe)Cl_3]$ and $[V(NC_6H_4Me)Cl_3]$, gave films with higher nitrogen content but only at temperatures above of 900 °C.[14]

We report here the dual-source CVD of vanadium nitride from vanadium(IV) chloride and hexamethyldisilazane (HMDS) under atmospheric pressure which yielded high-quality gold-coloured films of vanadium nitride. The reason for exploring HMDS as a nitrogen source was to try and avoid the problems in the conventional reaction of VCl_4 and NH_3 − which invariably lead to non-uniform films due to rapid gas-phase nucleation. Hexamethyldisilazane offers an alternative pathway by elimination of Me_3SiCl. The steric crowding in HMDS would also afford reduced rates of gas-phase combination and potentially better quality films. The VN films grown in this study show interesting properties that have potential to be used in glazing products for solar control applications.

Results

Vanadium(IV) Chloride with Hexamethyldisilazane (HMDS)

Synthesis

Reactions of vanadium(IV) chloride with hexamethyldisilazane (HMDS) under APCVD conditions at 300−550 °C yielded coatings of vanadium nitride on SiO_2-coated stand-

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Table 1. Experimental conditions and analytical results for the APCVD reaction of VCl_4 and HMDS

Deposition temperature [°C]	VCl_4 flow [mol min^{-1}]	HMDS flow [mol min^{-1}]	N_2 carrier gas flow rate [Lmin^{-1}]	Lattice parameter (a [Å])	Electrical resistivity [μΩ cm]
550	0.02	0.05	1.0	4.102(1)	380
500	0.02	0.05	1.0	4.092(2)	650
450	0.02	0.05	1.0	4.13(2)	800
400	0.02	0.05	1.0	amorphous	900
300	0.02	0.05	1.0	amorphous	4000

ard float glass. The reaction could be expressed, in the idealised form, as shown in Equation (1). This idealised equation does not take into account the thermal stability of Me_3SiCl which would almost certainly decompose to other materials under the CVD conditions.

$$VCl_4 + 2\,(Me_3Si)_2NH \rightarrow VN + 4\,Me_3SiCl + 1/6\,N_2 + 2/3\,NH_3 \qquad (1)$$

Flow rates of the precursor and plain nitrogen lines were varied. At total gas flow rates of 1.5 L min^{-1} or greater the films covered the whole substrate. However, at high carrier gas flow rates totalling over 3 L min^{-1} the deposition became non-uniform due to turbulence. For optimisation and coverage of all of the substrate in this particular APCVD setup, flow rates of 1 L min^{-1} for the plain nitrogen line and 0.3 L min^{-1} for the HMDS and 0.1 L min^{-1} for the VCl_4 line were used. This corresponds with molar flows of ca. 0.02 mol min^{-1} of VCl_4 and 0.05 mol min^{-1} of HMDS.

Characterisation

The films were analysed using glancing angle XRD, sheet resistance, SEM, EDAX, XPS, contact angle, Raman and UV/Vis reflectance and transmission measurements, selected data is given in Table 1. Film quality has been primarily correlated to deposition temperature and gas concentrations.

Films of uniform thickness were deposited over the entire substrate for a range of temperatures from 300 to 550 °C. The onset of deposition was noted at 300 °C as no film could be grown at 250 °C. The films were gold-coloured and free of pin-hole defects. The films could not be removed by rubbing with a tissue, soft cloth or scratched with a brass stylus or steel scalpel, indicating that they were extremely hard and typical of metal nitride films.[16] The vanadium nitride films were also unchanged by immersion in water, propan-2-ol, acetone, petroleum spirit and dilute (2 M) mineral acids for 48 h.

The glancing angle XRD analysis showed the presence of crystalline VN as the only detectable phase present in the films prepared at 450−550 °C.[17] The peaks were broad with the (2 0 0) peak being the most intense one, indicating a degree of preferred orientation. These films have a lattice constant from 4.09(2) to 4.13(2) Å (Table 1). This can be compared to the literature values where $VN_{1.00}$ films have a lattice constant recorded as a = 4.14(1) Å.[18] Bulk $VN_{0.92}O_{0.11}$ has an NaCl (*Fm3m*) structure and a lattice constant of a = 4.12 Å.[19] Previous work on the APCVD reaction of VCl_4 and NH_3 produced thin films of composition from $VN_{0.80}O_{0.18}$ to $VN_{0.68}O_{0.42}$ with lattice parameters of 4.078−4.072 Å. Notably in all of these studies the higher lattice constants were associated with the better nitrided products.

EDAX analysis confirmed the presence of vanadium and nitrogen in the films, although accurate quantitative data were not available due to the N peak being partially obscured by the vanadium. The EDAX measurements also showed breakthrough to the underlying substrate, thus making an accurate determination of any oxygen contaminant difficult. SEM analysis showed fine sub-micron spheroid particles of a uniform size distribution in the region of 250 nm (Figure 1). Growth rates as calculated from side-on SEM work were 175 nm min^{-1} at 450 °C and 250 nm min^{-1} at 550 °C.

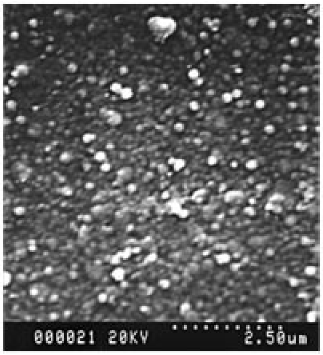

Figure 1. SEM of the films produced from the reaction of VCl_4 with HMDS at 550 °C

XPS analysis showed a small overlayer of oxide on all the VN samples, this was removed on Ar^+ etching. After the first few etchings the oxygen content was significantly reduced and the composition of the films prepared at 450, 500 and 550 °C had a V/N ratio of close to unity ($VN_{0.95(1)}$). This analysis also shows a surface N 1s binding energy shift at 396.9 eV and V 2p at 513.2 eV. These match previous measurements on VN.[20] the oxygen found in these films is a result of post CVD surface oxidation. This is because the oxygen content decreases with XPS sputtering depth and virtually disappears. This surface oxidation seems to be self-limiting as the VN films show no change in composition or in optical properties after storage in air for two years.

The VN films are highly reflective and the spectra show a strong reflection in the NIR beyond 600 nm. This is more pronounced for films laid down at the higher deposition temperatures. These VN coatings prepared at 500 and 550 °C show good heat-mirror properties and suggest that these films have potential application as solar control coatings where visible light is transmitted but IR radiation is reflected. At deposition temperatures below 450 °C the films show little reflectance in the NIR. Films deposited at this temperature and below had a matte appearance and were not as shiny. The morphology of the films was identical to that grown at higher temperatures − it would seem that it is the lack of crystallinity that accounts for the observed changes in the reflection properties of the films. The transmission spectra of the films prepared at 450−550 °C showed few features transmitting light across the majority of the visible spectrum, (Figure 2). Notably no pin-hole defects were detected by optical microscopy or SEM in these films.

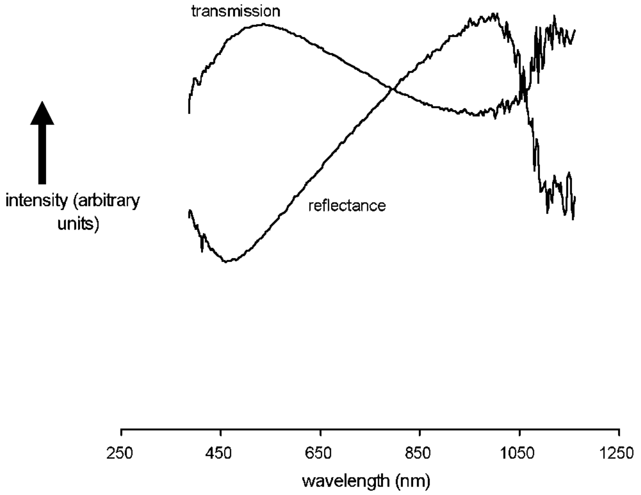

Figure 2. Transmission and reflectance spectra of films produced from the reaction of VCl_4 with HMDS at 550 °C

Raman analysis showed broad bands between 50 and 300 cm^{-1} that correspond to the region in which a powdered vanadium nitride standard gave a broad signal. Apart from this the Raman spectra were featureless. This indicates the absence of vanadium oxide phases (V_2O_5, VO_x, VO_2 and V_2O_3) and graphitic carbon in the films; as these are particularly strong Raman scatterers and would be expected to dominate the spectra even at low concentrations.

The electrical resistivity of the VN films was inversely proportional to the temperature of deposition. Post-treating the VN films with HMDS does not change the electrical resistivity of the film produced. The electrical resistivities of the films can be correlated with the powder XRD analysis − that is the resistance decreases with an increase in crystallite size (from amorphous at a deposition temperature of 300 °C to ca. 400 Å at 550 °C). The electrical resistivities measured of 380−4000 µΩ cm were similar to sputtered VN films (Table 1).[5]

The contact angles for water droplets of these films were calculated to be between 80 and 95° which indicates that the films were hydrophobic. The contact angle value for the silica-coated plain float glass was 75°.

Vanadium Oxychloride with Hexamethyldisilazane

Synthesis and Characterisation

Films produced from the reaction of vanadium(V) oxychloride with HMDS under APCVD conditions were dark-grey in colour. An idealised form of the reactions is given in Equation (2).

$$VOCl_3 + 2\,(Me_3Si)_2NH \rightarrow VN + 2\,Me_3SiCl + (Me_3Si)_2O + 1/2\,N_2 + HCl \quad (2)$$

Although some shiny areas were produced, the bulk of the films had a matte (lustreless) appearance. Substrate temperatures of 250−575 °C were employed in the deposition of these films in an attempt to improve uniformity of the surface and reduce the matte appearance. Despite this, most of the films were inhomogeneous and no correlations could be drawn as to what conditions favoured formation of the matte over shiny areas.

Powder XRD analysis of the films formed from $VOCl_3$ and HMDS showed slightly different data to the VCl_4 films. A cubic VN or oxynitride phase was identified and the measured lattice parameters a were from 4.07(9) to 4.08(0) Å. A second phase was also noted of V_2O_3.[21,22] This result is somewhat surprising as the analogous reaction of $VOCl_3$ and NH_3 yielded just a single-phase vanadium oxynitride material and not a biphasic mixture.

The XPS analysis gave a compositional ratio of $V_{3.0}N_{1.0}O_{4.0}$ for the film prepared from the reaction of $VOCl_3$ and HMDS at 600 °C which is consistent with the film consisting of two species V_2NO and V_2O_3. This correlates with the literature where treatment of V_2O_5 with ammonia at temperatures above 600 °C yielded a mixture of V_2NO and V_2O_3.[25] The V_2NO was reported to be black and have a cubic (*Fm3m*) structure which agrees with the XRD results.[23] Binding energy shifts for V 2p were at 513.5 eV, N 1s at 396.8 eV and O 1s at 530.7 eV which are in agreement with previous results.[17] The V 2p and O 1s peaks were much broader than that obtained for the XPS analysis of the films formed from VCl_4 and HMDS and was consistent with two environments (oxide and oxynitride).

The Raman spectra of the films formed from $VOCl_3$ and HMDS show a broad band at the lower wavenumbers similar to the samples produced from VCl_4 and HMDS. An additional broad band in the spectra was observed and assigned to the presence of a vanadium oxide phase reinforcing the XPS and XRD results (Figure 3). The additional Raman peaks associated with V_2O_3 were more defined in the matte area of the coatings.

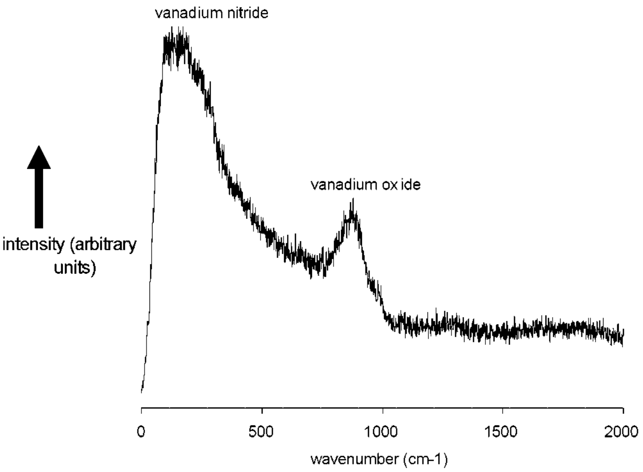

Figure 3. Raman spectrum of film produced from the reaction of $VOCl_3$ with HMDS

Reflectance spectra showed that certain of these samples reflect in the NIR although this extended across the visible as well. This was most apparent for the reflective areas of the films. The transmission spectra were noisy and, although they transmitted light across the visible, they also had transmission in the IR region showing that these films are not of sufficient quality for heat-mirror applications.

The majority of these films were conducting although their resistivity was an order of magnitude higher than the films formed from the reaction of VCl_4 with HMDS. There was difficulty in finding a correlation between deposition conditions and resistivity values of the film and few conclusions could be reached regarding the production of better quality deposition. The resistivity readings changed dependent on the area under analysis on the same film. Resistivity was noted to be greater on the matte regions of the film.

Contact angle measurements of these films for water droplets were contrasting depending on the area of film analysed. The shiny areas were measured in the region of 80° which is similar to that of the films from the reaction of VCl_4 with HMDS. However, values as low as 28° were recorded on the areas that were blackened, suggesting the presence of a vanadium oxide phase which has a lower contact angle. Measurements in these areas was not as simple as the shiny areas and open to error due to the presence of solid deposits on the surface of the films. Indeed, the irregular porous surface structure could be responsible for the lowered contact angle.

Discussion

Reaction of vanadium(IV) chloride with hexamethyldisilazane under APCVD conditions produced vanadium nitride films with good optical characteristics – free of pinhole defects, reflecting in the NIR and transmitting in the visible. This demonstrates that these films have potential to be used as heat-mirror coatings on window glass. To be effective in this application the coating needs to have good transmission in the visible region whilst providing high reflectance in the IR.[24] This means that the heat mirror would enable a householder to see out of the window but not be subject to heat-gain from the IR part of the solar spectrum. Few materials have this combination of properties.

Less ideal reflectance and transmission spectra from the VN samples deposited at lower temperatures can be explained by lower crystallinity. This is confirmed by the resistivity measurements and the glancing angle XRD data, where samples deposited at temperatures above 450 °C gave an XRD pattern typical of a crystalline material and had considerably lower resistivity values. The SEM analysis shows that these films are composed of fine particles.

In comparison with films produced from the standard dual-source reaction of VCl_4 with ammonia, the films deposited from the APCVD reaction of VCl_4 with HMDS have superior qualities. In the former case, fast pre-reaction led to blockages of the pipework and gas-phase nucleation caused pin-hole defects in the films. Films formed from the dual-source reaction of VCl_4 with HMDS gave uniform coverage of the substrate and were free from pin-hole defects. These films were also gold-coloured whereas the VCl_4/NH_3 reaction under comparable conditions produced less reflective brown-yellow films. The reaction between VCl_4 and HMDS is probably less rapid than VCl_4 and NH_3 due to the size of the $SiMe_3$ groups. The absence of Si and C in these films suggests that the elimination of Me_3SiCl is facile, providing the driving force of the APCVD reaction [Equation (1)]. Notably a large excess of HMDS is not required to form VN films, just a slight excess over the gas-phase concentration of the vanadium tetrachloride (1:2.5). In nitride preparation from a metal halide and ammonia typically a hundredfold excess of ammonia would be used. The VN films formed in this work were superior in optical properties to those prepared from the analogous reaction with ammonia.

The films produced from the reaction of vanadium oxychloride and HMDS gave unexpected results. These were dark grey and, although the majority were conducting, the resistivity values were significantly higher than those of the samples produced from VCl_4. The reflectance and transmission spectra from these samples showed poorer heat-mirror properties and, although certain patches of these films were hard and adhered to the substrate, larger areas appeared to consist of powdery deposits and were more easily removed from the substrate. The Raman data shows that these films are contaminated with carbon and vanadium(III) oxide. This result was confirmed by XRD and by the compositional analysis by XPS. This suggests that significant amounts of oxygen remains bound with the vanadium from the vanadium oxychloride precursor during the reaction with HMDS. Interestingly, these results contrast with the reactions with $VOCl_3$ and NH_3 which formed a single-phase oxynitride product rather than a mixed-phase material.[15] This is probably a consequence of involving the $SiMe_3$ as a leaving group in the reaction. However, further speculation is not warranted at this stage as to the detailed reaction mechanism.

Conclusion

Vanadium(IV) chloride reacts with hexamethyldisilazane under APCVD conditions to form uniform gold-coloured films that have optical properties suitable for heat-mirror applications. These films have a composition of $VN_{1.0}$. This has proved to be a novel and efficient method of producing VN films utilising existing technology. This method produces more uniform films free of pin-hole defects compared to the current method of treating VCl_4 with ammonia. It should also be noted that multi-precursor CVD normally requires a large excess of one of the reactants and by using hexamethyldisilazane as the nitrogen source this is overcome as a more complete reaction is occurring. Although a silicon-containing precursor is utilised in these depositions, no evidence of silicon is found in the resulting films.

The APCVD reaction of $VOCl_3$ with HMDS gave non-uniform grey-black films with a higher electrical resistivity than the gold-coloured VCl_4/HMDS films. These films consist of an oxynitride (V_2NO) and V_2O_3.

Experimental Section

Vanadium(IV) chloride, vanadium(V) oxychloride and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were purchased from Aldrich Chemical Company and used without further purification. The HMDS was loaded in one bubbler and the vanadium precursor was loaded into a second bubbler. Standard float glass with a silica diffusion barrier coating was used for the following deposition studies. The glass was cleaned thoroughly prior to use with water followed by propan-2-ol then dried at room temperature in a vertical position. Nitrogen (99.9% BOC) was used as the carrier gas after being passed through an oxygen removal column (CuH). The pipe assembly, bubbler and experimental setup are fully described elsewhere.[20,25] For this series of deposition experiments three independently controlled gas streams – the vanadium source, HMDS and nitrogen – are passed into a mixing chamber prior to entering the reaction chamber. The reactor is a cold-wall design similar to those reported by us previously.[18] The substrate is heated on a graphite-block containing a single Whatman cartridge-heater. The glass is coated in a horizontal position and has dimensions of 15 cm × 4 cm × 0.3 cm. The temperature of the glass substrate was recorded using an independent thermocouple and compared to the setting of the controlling thermocouple. It was found that there was a temperature variation across the surface of the glass substrate of ca. 40 °C. All temperatures recorded for the depositions in this report are those of the hottest central part of the glass substrate. Substrate temperatures ranged from 250 to 575 °C. All coatings were carried out at atmospheric pressure for 2 min. A range of flow rates for all three gas lines was used. Glancing angle X-ray diffraction analysis of the films was obtained using a Siemens D5000 diffractometer in the reflection mode (1.5° incidence) using Cu-K_α (1.5406 Å) radiation. SEM/EDAX was determined with a JEOL CR-37. XPS was performed with a VG ESCALAB 220i XL using focused (300 μm spot) monchromatic Al-K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 100 meV. A flood gun was used to control charging and the binding energies were referenced to an advantageous C 1s peak at 284.6 eV. Depth profiles were obtained by using an argon sputtering-gun. Reflectance and transmission spectra were recorded between 300 and 2600 nm with a U4000 spectrophotometer and between 300 and 1150 nm with a Zeiss miniture grating spectrometer. Raman spectra were obtained with a Renishaw 1000 spectrometer using an Ne excitation laser line. Contact angle measurements were determined by measuring the spread of a 1 μL^3 droplet of water. A powder sample of vanadium nitride (99%) was purchased from Aldrich Chemical Co. and used for comparison purposes for Raman spectroscopy.

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