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# Atmospheric pressure chemical vapour deposition of vanadium nitride and oxynitride films on glass from reaction of $VCl_4$ with $NH_3$

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Atmospheric pressure chemical vapour deposition of vanadium nitride and oxynitride coatings was achieved on glass substrates from the reaction of $VCl_4$ and $NH_3$ at 350–650 °C. The coatings show excellent uniformity, surface coverage, adherence and a range of colours (yellow, blue–silver) dependent on deposition temperature and film thickness. Growth rates were of the order of 1 μm $min^{-1}$. All films deposited at greater than 450 °C were crystalline, single phase with an fcc NaCl diffraction pattern, $a = 4.065–4.116(2)$ Å. Scanning electron microscopy (SEM) revealed different film thicknesses and surface morphologies consistent with an island growth mechanism. X-Ray photoelectron spectroscopy (XPS) revealed that individual samples were homogeneous. Compositional variations between films were related to reaction conditions; $VN_{0.8}O_{0.18}$–$VN_{0.56}O_{0.8}$. XPS binding energy shifts were seen for V 2p at 513.3 eV for O 1s at 530.8 eV and for N 1s at 397.1 eV and were largely invariant between samples. Energy dispersive X-ray analysis (EDXA) and electron probe studies gave elemental ratios that were in agreement with the XPS measurements, indicating no chlorine incorporation. Raman spectra showed a broad band at 600 $cm^{-1}$. Sheet resistance measurements indicated that all films were metallic. Optically, the films were reflective in the range 800–2600 nm and showed reasonable transmission in the range 300–800 nm. The films show promise as solar-control coatings.

## Introduction

Atmospheric pressure chemical vapour deposition (APCVD) is a technique widely used to coat a substrate such as glass or a metal with a thin film.[1] These films have a variety of properties such as oxidation resistance, colour and reflectivity that modify the properties of the substrate. We are interested in forming solar-control coatings on glass that could be utilised for window environmental management.[2] These coatings have a unique combination of transmission and reflection properties that enable passage of visible light through the coating but are highly reflective at IR wavelengths; when placed on a window the coating allows sunlight through a window but reflects back into the building black-body energy.[3] European legislation requires that glass being used in new buildings must contain some form of solar control coating; this is provided at present by CVD prepared F-doped tin oxide and tin doped indium oxide.[4] Some metal coatings such as copper, silver and gold also function effectively as solar control coatings. These metal coatings have limited application due to chemical and wear resistance.[5]

Metal nitrides have been proposed as a potential new class of solar control coatings.[6] Thin films of titanium nitride have reasonable optical transparency and good IR reflective properties. The nitride films are also extremely wear resistant. Titanium nitride has attracted the most attention as a coating and numerous single source CVD methods have been developed for its synthesis. Titanium nitride has been deposited by APCVD from $Ti(NR_2)_4$ (R = Me, Et) with and without the addition of ammonia.[7] In the temperature range 400–700 °C it has been deposited from the reaction of $TiCl_4$ and ammonia.[8] At high substrate temperatures TiN films have been grown from $TiCl_4$ and a nitrogen/hydrogen mix (1100 °C).[9] The other early transition metal nitrides, including VN, NbN, TaN, HfN, ZrN all have predominant fcc-NaCl phases with similar properties to TiN.[10] There are comparatively fewer reports of the growth of these latter materials by CVD. Vanadium nitride has been prepared from the reaction of $V(NMe_2)_4$ and ammonia forming thin films that are polycrystalline and slightly nitrogen rich.[2] Notably minimal oxygen or carbon contamination (*ca.* 15 atom%) was found in the films. Vanadium nitride films have also been grown by other techniques such as $N_2/H_2$ plasma processing,[11] ion beam assisted deposition,[12] magneton sputtering,[13] molecular organic CVD[14] and pulsed laser deposition.[15] In most nitride CVD the incorporation of oxygen in the films either from the substrate or processes gases has proved problematic.[16] Films have been classified as metal nitrides even with 30 atom% oxygen or carbon. It is known that oxygen contamination can be detrimental to the hardness, conductivity and diffusion barrier properties of transition-metal nitride coatings. However the optical properties of the nitrides are not significantly altered by the presence of oxygen.[17]

In this paper we report the reaction of $VCl_4$ and $NH_3$ by APCVD to form vanadium nitride films. These films show the potential to function as a new class of solar control coatings.

## Experimental

Vanadium chloride was purchased from Aldrich Chemical Co. and used without further purification. Standard float-glass that had been treated with an SiCO diffusion barrier layer was used for the deposition studies. The glass was cleaned prior to use by washing with petroleum ether (bp 60–80 °C) and isopropyl alcohol followed by drying in air in a vertical position. The ammonia (99.99%, BOC) was used as supplied; nitrogen (99.9%, BOC) carrier gas streams were dried over molecular sieves (200 °C) and passed through an oxygen removal column (CuH) prior to entering the system. A schematic diagram of the pipe assembly is given in Fig. 1. All pipes were made from 1/2 or 1/4 inch i.d. stainless steel and wrapped in heating tape. Control of the pipes, reactor and bubbler temperatures was achieved by ten independent type K and R thermocouples. This

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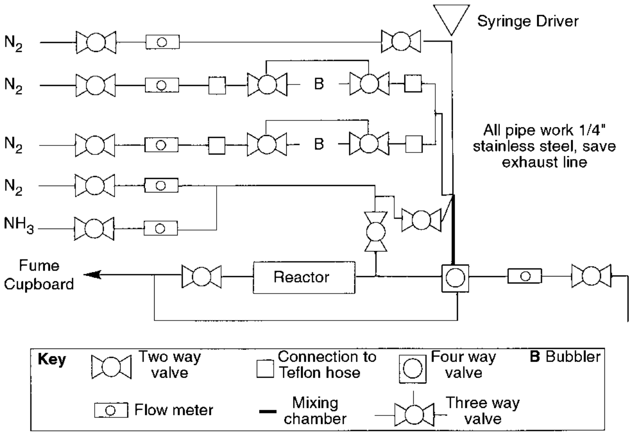

**Fig. 1** Schematic diagram of the pipe work assembly used in the APCVD experiments.

system allows three independently temperature controlled gas streams to converge through a four-way valve prior to entering the reactor chamber. A nitrogen/ammonia flow line was set up to mix with the reactive gas stream 4 cm from the APCVD cold-wall reactor chamber. The reactor-chamber heater consisted of a horizontal graphite-block that was heated internally by three Whatman cartridge heaters. The glass used had dimensions 225 × 90 × 4 mm. Precursors were placed into one of two bubblers, Fig. 2. Detailed diagrams of the reactor chamber have been published previously.[18] Gas handling lines were typically baked out under flowing nitrogen for 1 h at 150–200 °C prior to deposition. The central reactor was brought to the required reaction temperature for at least ten minutes before each run. Prior to each coating the nitrogen supply was diverted through the heated precursor for several seconds and the precursors vented to waste. The APCVD experiments were initiated such that the precursor entered the line to the chamber, mixed with the gas from the ammonia–nitrogen line and entered the reactor. All coatings were carried out at atmospheric pressure for between 20 and 120 s. After each run the precursors were initially diverted to waste and then the gas stream diverted away from the precursor bubblers. The assembly was allowed to cool under nitrogen until *ca.* 50 °C when the coated glass was removed from the reactor. Occasionally the pipework blocked due to pre-reaction of the gases prior to entering the coater. Typical flow rates and temperature of runs are summarised in Table 1.

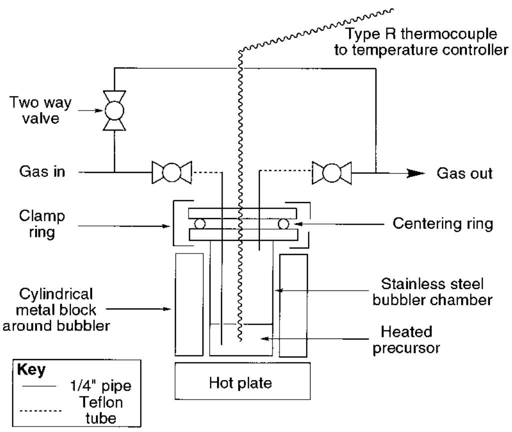

**Fig. 2** Schematic diagram of precursor containers, "bubblers".

Glancing angle X-ray analysis of the films was obtained on a Philips X-pert diffractometer using unfiltered Cu-Kα radiation ($\lambda_1 = 1.5405$ Å, $\lambda_2 = 1.5443$ Å) in the reflection mode at a glancing incident angle of 1.5°. Samples were indexed using Unitcell and compared with database standards.[19] The crystallite size was estimated using the broadening of the (2 0 0) reflection using the Scherrer equation and ignoring any effects from lattice strain. SEM/EDAX was undertaken on a Hitachi SEM S-570. Electron probe analyses were conducted on a JEOL EMA using polished samples and compared to standards. XPS was performed with a VG ESCALAB 220i XL using focused (300 µm spot) monochromatic Al-Kα 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 adventitious C 1s peak at 284.4 eV. Depth profiles were obtained by using an argon-sputtering gun. Elemental compositions were determined by integrating the peak areas from the XPS spectra and applying appropriate significance factors (correlated with standards). Reflectance and transmission spectra were recorded between 300 and 2600 nm on a Hitachi U4000 spectrophotometer. Measurements were standardised relative to a rhodium mirror (reflectance) and vacuum (transmission). UV spectra were recorded on a Helios double beam spectrometer. 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.

## Results

Reaction of anhydrous vanadium chloride with ammonia under APCVD conditions at 350–650 °C was shown to form coatings of vanadium nitride, Table 1, eqn. (1). In all cases

**Table 1** APCVD reaction conditions; XPS, XRD and sheet resistance measurements on the $VN_xO_y$ films on glass prepared from the reaction of $VCl_4$ and $NH_3$

| Growth time/s | Deposition temperature/°C | $NH_3$ flow/dm$^3$ min$^{-1}$ | Process gas flow/dm$^3$ min$^{-1}$ | XPS composition | Lattice parameter/Å | Crystallite size/Å | Sheet resistance/Ω □$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 30 | 350 | 0.5 | 5 | $VN_{0.56}O_{0.85}$ | [b] | [b] | 2450 |
| 30 | 450 | 0.5 | 5 | $VN_{0.68}O_{0.42}$ | 4.072 | 170 | 80 |
| 30 | 550 | 0.5 | 5 | $VN_{0.77}O_{0.51}$ | 4.078 | 195 | 60 |
| 30 | 650 | 0.5 | 5 | $VN_{0.68}O_{0.63}$ | 4.088 | 200 | 175 |
| 30 | 500 | 0.2 | 10 | $VN_{0.65}O_{0.80}$ | [c] | [c] | 240 |
| 30 | 500 | 0.4 | 10 | $VN_{0.66}O_{0.46}$ | 4.070 | 150 | 170 |
| 30 | 500 | 0.6 | 10 | $VN_{0.66}O_{0.40}$ | 4.070 | 190 | 115 |
| 30 | 500 | 0.8 | 10 | $VN_{0.78}O_{0.32}$ | 4.071 | 215 | 115 |
| 30 | 500 | 1.0 | 10 | $VN_{0.80}O_{0.18}$ | 4.074 | 225 | 115 |
| 30 | 450 | 0.5 | 10 | $VN_{0.78}O_{0.51}$ | 4.065 | 220 | [c] |
| 20 | 500 | 0.8 | 10 | $VN_{0.75}O_{0.31}$ | 4.082 | 205 | 205 |
| 60 | 500 | 0.8 | 10 | $VN_{0.75}O_{0.30}$ | 4.082 | 205 | 400 |
| 120 | 500 | 0.8 | 10 | $VN_{0.75}O_{0.31}$ | 4.082 | 205 | 70 |
| 30 | 350[a] | 0.5 | 10 | $VN_{0.80}O_{0.25}$ | 4.116 | 175 | 29 |

[a] Annealed under ammonia. [b] Amorphous. [c] No data recorded.

oxygen was incorporated in the films.

$$6VCl_4+8NH_3\rightarrow 6VN+24HCl+N_2 \qquad (1)$$

The films were analysed by glancing angle X-ray powder diffraction, XPS, sheet resistance, SEM/EDAX, electron microprobe, Raman and optical transmission/reflectance measurements. Film quality and thickness were correlated with deposition temperature, run-time, precursor temperature and gas flow rates.

All the films prepared from the APCVD of $VCl_4$ and $NH_3$ were uniform, coloured, adhesive and impervious to 48 h immersion in common solvents (water, ethanol, acetone, toluene) and dilute mineral acids. Film colour was largely dependent on thickness with the thinnest films (20 s deposition) appearing yellow and the thickest films (120 s) blue–silver. Visual inspection of all of the films showed that they were reflective with some optical transmission. Growth rates were typically 1 μm min$^{-1}$ at a substrate temperature of 500 °C as assessed by SEM measurements. Apart from the film deposited at 350 °C all of the films were conductive showing sheet resistance measurements in the range of 60–250 Ω □$^{-1}$.

Glancing angle X-ray diffraction showed that films prepared at 450–650 °C were crystalline. In all cases only a single phase was observed that could be indexed to a cubic NaCl fcc-lattice type with lattice spacings in the range 4.065–4.116 Å. Some preferred orientation of growth in the 2 0 0 direction was noted, Fig. 3. Thin films of VN have reported lattice constants of 4.14(1) Å;[20] bulk $VN_{0.11}O_{1.2}$–$VN_{0.92}O_{0.11}$ materials have lattice constants from 4.076–4.128 Å.[21] Crystallite sizes of 175–225 Å were estimated from line broadening studies.

SEM showed that the films were uniform and were consistent with an island growth mechanism. Electron probe line analysis showed uniform composition across various line scans and EDAX showed uniform composition across a number of surface spots. Neither technique showed any chlorine incorporation in the films even at the lowest deposition temperature of 350 °C. Only vanadium, nitrogen and oxygen were observed. Quantification of the nitrogen and oxygen using these X-ray analysis techniques was complicated because they are the limit of the instrumental detection (boron cut off) and the lower energy X-rays emitted by these elements are partly absorbed by the film. This gives rise to poor quantification. However the results were in broad agreement with those obtained from XPS analysis.

XPS depth-profiles showed no chlorine contamination. All of the depth-profile studies showed changes in composition with depth. At the surface some carbon and oxygen was observed corresponding to adsorbed dioxygen and carbon dioxide, these were removed on the first etching. On subsequent etches a bulk uniform composition was obtained, as shown in Table 1 and Fig. 4. Bulk composition showed vanadium, nitrogen and oxygen as illustrated in Fig. 5. Binding energy measurements obtained after depth profiling were typically V 2p at 513.3 eV; O 1s at 530.8 eV and N 1s at 397.1 eV. These values showed virtually no changes irrespective of film composition. The N 1s and O 1s binding energy values are as expected for a metal nitride (N 1s; 396.8–398.0 eV) and a metal oxide (O 1s; 529.5–531.3 eV).[17] A vanadium binding energy shift of 513.3 eV is intermediate between that of standard bulk VN (V 2p; 514.3 eV) and vanadium metal (V 2p; 512.14 eV).[22]

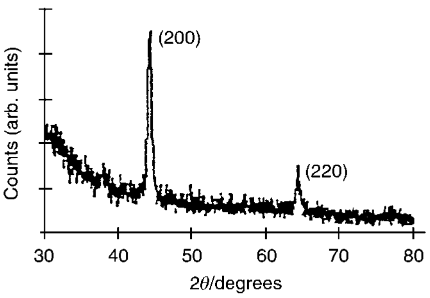

**Fig. 3** Glancing angle X-ray diffraction patterns from reaction of $VCl_4$ and $NH_3$.

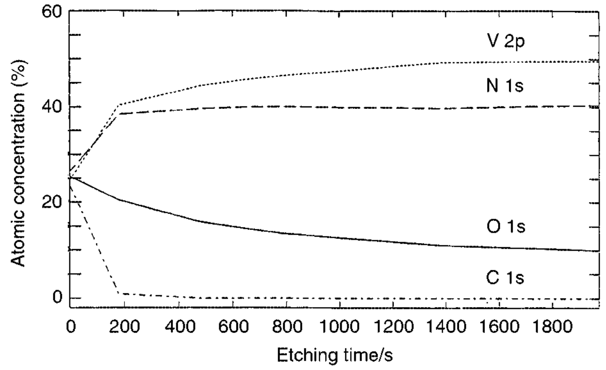

**Fig. 4** XPS depth profile analysis; percent of element present against sputtering time (*ca.* 10 nm min$^{-1}$).

Optical properties of the films were assessed in the region 240–2600 nm by reflectance and transmission measurements. All of the films grown by APCVD of $VCl_4$ and ammonia at temperatures >350 °C showed good reflection properties in the range 800–2500 nm, and lower reflectivity in the visible region, ideal for heat-mirror applications, Fig. 6. Reflectivity was maximised for films grown at high deposition temperatures, lower process gas flow rates and higher flows of ammonia. The reflectivity of the films was unrelated to growth times. The optical transmission properties of the films were dependent on film thicknesses. The best transmission properties were obtained for films with short growth times (30 s) and low flows of ammonia. The film grown for 120 s was virtually opaque and highly reflective.

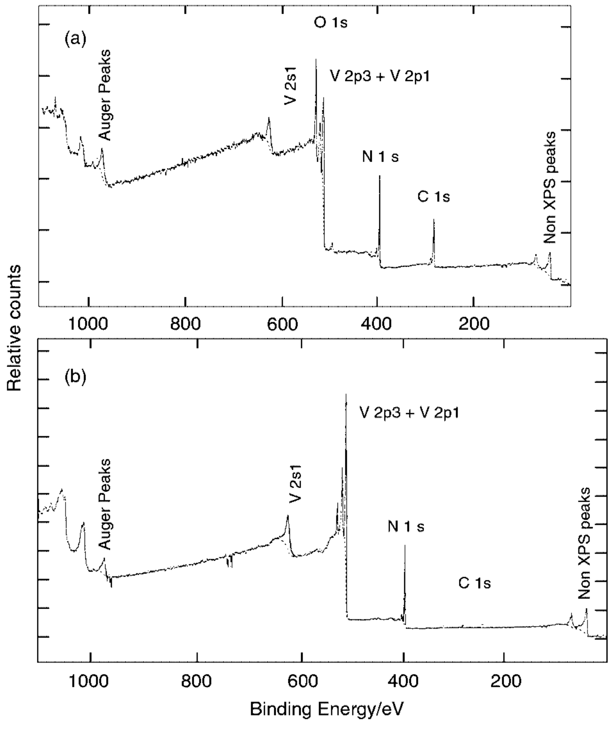

**Fig. 5** XPS scan of a film prepared from the APCVD of $VCl_4$ and $NH_3$ at 500 °C for 30 s ($NH_3$ flow of 1.0 dm$^3$ min$^{-1}$, $N_2$ flow of 10 dm$^3$ min$^{-1}$, $VCl_4$ flow of 0.42 dm$^3$ min$^{-1}$). (a) Initial survey spectrum, (b) after 45 min of argon etching, bulk composition.

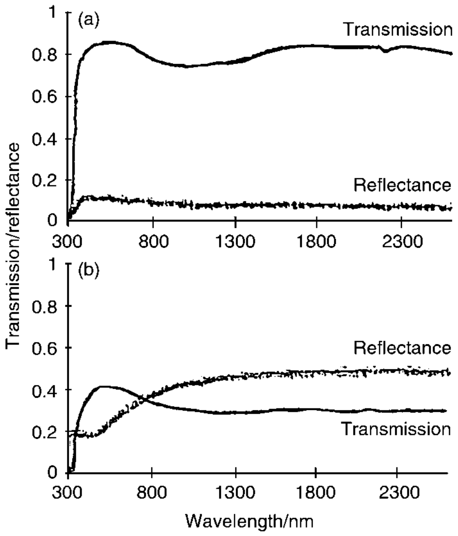

**Fig. 6** Reflectance and transmission measurements in the region 300–2500 nm for (a) plain glass, (b) plain glass coated with $VN_{0.8}O_{0.18}$ prepared at 500 °C for 30 s ($NH_3$ flow of 1.0 $dm^3$ $min^{-1}$, $N_2$ flow of 10 $dm^3$ $min^{-1}$, $VCl_4$ flow of 0.42 $dm^3$ $min^{-1}$). The *y*-axis value of 1 represents 100% reflectance or transmission.

Raman spectra of the films showed one broad band at *ca.* 600 $cm^{-1}$. The spectra of the oxygen rich and oxygen poor VN films were essentially identical.

## Discussion

APCVD reaction of $VCl_4$ with $NH_3$ at 350–650 °C forms vanadium nitride coatings that contain significant oxygen contents. No chlorine was found in the coatings, despite the use of a metal halide starting material. The presence of oxygen in the films is puzzling, XPS depth profiling indicates that the oxygen content in the films is greatest at the surface. However, this is readily reduced by sputtering to give an oxygen content that is maintained at a constant level through the bulk of the film. This indicates that oxygen incorporation in the films is unlikely to have arisen from diffusion of oxygen through the glass substrate. It is also unlikely that the oxygen content in the bulk of the films arose from handling and storage of the sample in air as a film that had been exposed to air for four months gave consistent bulk values of oxygen when reassessed by XPS. It is most likely that the oxygen came from the nitrogen process gas. Despite the nitrogen supply being 99.9% pure and being scavenged by an oxygen removal catalyst the residual oxygen was enough to introduce reliably and reproducibly a constant oxygen presence in the films. An alternative source of oxygen in the films is the presence of $VOCl_3$ in the $VCl_4$ supply. We have shown previously that $VOCl_3$ reacts with ammonia under APCVD conditions to form largely oxygen free films,[17] hence we tend to disfavour this as a route for oxygen incorporation. The oxygen content in the films grown in this study were lowered and the nitrogen content raised by using higher flows of ammonia; 2 atom% ammonia in the gas stream gave $VN_{0.65}O_{0.80}$ films whilst 10 atom% ammonia in the gas stream gave $VN_{0.80}O_{0.18}$ films. At all flow rates the ammonia was in at least a two fold excess over the $VCl_4$ precursor. Oxygen content also showed some variation with deposition temperature. At constant flow rates of ammonia the oxygen content was lowest for depositions at 450 °C. The oxygen content of the films could be significantly reduced by post annealing of the samples under a flow of 1 atom% $NH_3$ in nitrogen at 650 °C for 1 h. A sample prepared at 350 °C with a 5% $NH_3$ flow in nitrogen gave a composition of $VN_{0.57}O_{0.85}$. A similar sample that was post treated gave a bulk composition of $VN_{0.8}O_{0.25}$.

Apart from the film produced at 350 °C all of the films were crystalline and single phase. They indexed on a cubic cell with crystallite sizes in the range 150–225 Å. The oxygen incorporated in the films is not manifest as a secondary phase (such as $V_2O_3$). It is well known in bulk studies that oxygen can substitutionally replace nitrogen in metal nitride lattices. Vanadium nitride is an example of an interstitial nitride that has nitrogens placed within a closed packed metal lattice.[10] Vanadium nitride has a known composition range of $VN_{1.1}$–$VN_{0.7}$. In virtually all of the CVD produced films the vanadium metal has a formal oxidation state of V(III). A slight variation in oxidation state of vanadium is noted with oxygen content; the film with the highest oxygen content $VN_{0.56}O_{0.85}$ has a formal oxidation state of V(+3.4) whilst the film with lowest oxygen content $VN_{0.8}O_{0.18}$ has V(+2.76). In all cases this indicates a reduction of the vanadium from the starting material V(IV). No significant changes in the lattice constants were observed with composition. Typical lattice constants were 4.075(5) Å, Table 1. Significantly, the sample that was annealed under an ammonia flow for 1 h showed a larger lattice constant of 4.116 Å.

The vanadium nitride films show potential as solar control coatings, they all have good reflectivity in the IR region and a significant dip in reflectivity in the visible region. Transmission through the films is reasonable and directly correlated with film thickness. Changes in oxygen content in the films had negligible effects on the colour of the films and the reflectance/transmission properties. Notably the optical properties of the films showed no variation after exposure to air for three years. The optical properties displayed by these films are comparable to TiN.

## Conclusions

Thin films of VN containing variable oxygen content have been grown by APCVD on glass substrates at 350–650 °C. The films showed negligible carbon and chlorine contamination and at best a composition of $VN_{0.8}O_{0.18}$. The oxygen content within the films arises from contamination from the nitrogen carrier gas stream; it can be reduced by increasing the flow of ammonia in the system or by post annealing in a dilute ammonia atmosphere. Films are adhesive, scratch resistant and impervious to common solvents and dilute acids. They show no alteration in optical properties after storage in air over a three-year period. The coatings have some potential as heat mirror coatings as they are largely optically transparent in the visible and reflective in the infrared.

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