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Full Paper

An Investigation of Titanium-Vanadium Nitride Phase Space, Conducted Using Combinatorial Atmospheric Pressure CVD

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The technique of combinatorial atmospheric pressure (AP)CVD, a recent addition to the growing number of combinatorial materials methods, is used to form twelve members of the $Ti_xV_{1-x}N$ alloy series with $0.29 < x < 0.94$. This series of compounds has a rock-salt structure with TiN and VN as the end members. The twelve phases, which have potential use as heat mirror coatings, are all synthesized in a single experiment. The structure and properties of the materials are investigated using powder X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The optical properties are considered using visible-IR spectroscopy (IRS), which allows the suitability of the films as solar control coatings to be investigated and optimized as a function of composition.

Keywords: APCVD, Combinatorial, Heat mirror, Titanium nitride, Vanadium nitride

1. Introduction

Combinatorial chemistry is a synthetic method by which a large number of similar, but systematically differing, compounds are made simultaneously. This generates a library of compounds which can then be screened for a desired property. The method was pioneered in the 1960s in peptide synthesis,^[1] and has since become a mainstay of the pharmaceutical industry.^[2] The advantages that have made the technique popular in drug manufacturing—rapid synthesis and analysis of a large number of compounds simultaneously—have also attracted workers in the field of thin film synthesis looking to identify new phases, or optimize synthetic conditions.^[3–5] Some of this work has borrowed the microreactor concept originally used in combinatorial work,^[3,6] while other workers have focused on an alternative strategy in which a continuous film is laid down onto a substrate, but with two or more reagent gradients across it, leading to an overall compositional gradient across the substrate.^[7,8] Measuring the properties of the film at discrete points across this gradient allows the varying phase space, present across the substrate, to be investigated. Our group has recently shown that this strategy can be used in APCVD.^[9]

In the work presented here, we show that combinatorial APCVD can be used to investigate the titanium-vanadium

nitride system. Previous work has shown films of TiN can be deposited from $TiCl_4$ and NH_3 ,^[10] and films of VN from VCl_4 and NH_3 .^[11] Both VN and TiN have the rock-salt structure, with similar lattice parameters, and $Ti_xV_{1-x}N$ alloy phases have been reported.^[12] By supplying the precursors asymmetrically into the reactor through separate entry points, we show that it is possible to generate a film with composition varying laterally across the substrate from VN to TiN with a range of $Ti_xV_{1-x}N$ compositions spread evenly between $0.29 < x < 0.94$ —effectively allowing twelve points in the $Ti_xV_{1-x}N$ phase space to be investigated in a single experiment. The compositional spread was analyzed at these discrete points using XRD mapping,^[13] and the chemical composition determined by wavelength dispersive X-ray (WDX) analysis.

The $Ti_xV_{1-x}N$ system was chosen for this investigation because both end members (TiN and VN) have a number of potential industrial applications. Titanium nitride is used as a decorative gold-colored coating and a wear-resistant coating.^[14] Reports have also shown that the hardness, and hence effectiveness of wear resistance, of TiN can be increased by the substitution of vanadium into these phases.^[15,16] Attempts have also been made to investigate the optimum level of vanadium substitution, by producing up to seven members of the solid solution, but with each phase being made in a discrete synthesis.^[15]

The $Ti_{1-x}V_xN$ system is ideal then for a combinatorial investigation, as a solid solution is known to exist in which the physical properties of the end members can be improved upon in the intermediates. In addition to wear resistance properties, both TiN and VN have been identified as potential heat-mirror coatings.^[17–19] A heat mirror reflects the near-IR of the solar spectrum, while allowing the transmission of visible light, and can be used as window

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coatings to help control the uptake of solar energy in tropical climates.^[20] The effectiveness of both TiN and VN as heat mirrors has been investigated previously,^[21,22] but members of the $Ti_{1-x}V_xN$ system have not yet been considered. Thus the combinatorial investigation presented here has allowed the heat-mirror properties of the alloy system to be investigated, and this property to be investigated as a function of composition.

2. Results and Discussion

A combinatorial spread of phases was formed across a substrate by overlapping parallel gas streams of VCl_4 and $TiCl_4$ with NH_3 , to form a film of metal nitride, with strips of TiN and VN on either side of the substrate, and a mixed $Ti_xV_{1-x}N$ section in the centre where the gas streams overlap. Analysis of the side-on scanning electron microscopy (SEM) images found that the thickness varied from 930 to 4150 nm, giving varying growth rates of 30 to 140 nm s^{-1} .

The phase composition of the film was confirmed by PXRD. A line of sixteen points, perpendicular to the gas-flow direction and 90 mm in from the leading edge of the film, had diffraction patterns recorded at 5 mm intervals to cut across the expected regions of differing composition. It was found that twelve of the patterns showed this differing composition, as determined by variation in peak position. These patterns are shown in Figure 1. The peaks in all of the patterns could be indexed using the $Fm\bar{3}m$ space group with a different lattice parameter, a , found for each spot varying smoothly in the range 4.13–4.21 Å depending on the position across the substrate. This is consistent with the hypothesis that a compositional spread has been formed as the titanium-vanadium metal nitrides are known to crystallize in the rock-salt structure with space group $Fm\bar{3}m$ and with lattice parameters of the postulated end members of the series of 4.09 Å for VN and 4.23 Å for TiN.^[23] Figure 2 shows a plot of the indexed lattice parameter against substrate position for the twelve indexed patterns.

The chemical composition of each of the investigated spots was determined by EPMA. This was carried out by measuring six different spots within a 1 mm diameter range

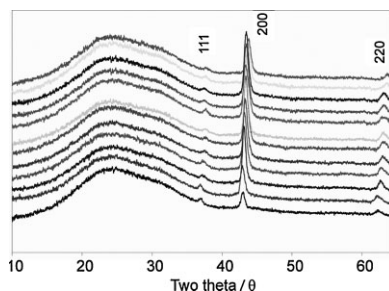


Fig. 1. The twelve diffraction patterns indexed in $Fm\bar{3}m$, recorded at intervals of 5 mm perpendicular to the direction of precursor gas flow. The variation in peak position is seen most clearly in the 220 peak.

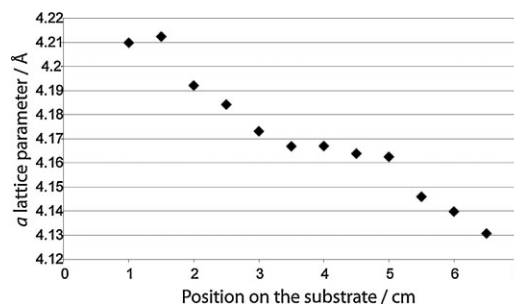


Fig. 2. Plot of the lattice parameter taken from the indexed diffraction pattern, against the position on the substrate.

of the selected point on the substrate, and averaging the composition across these six different spots to determine the value for that point. Due to an unfortunate overlap of the nitrogen K line with the titanium L line in the X-ray spectra, the nitrogen content of the film could not be directly quantified. This did not effect the quantification of Ti itself, as this is determined using the Ti K lines, which are not overlapped by peaks of any of the other elements present. The deposited films were also sufficiently thin that peaks due to the elements present in the underlying glass substrate could also be detected, so the oxygen content of the film also could not be reliably determined. It should also be noted that no chlorine was detected by the chemical analysis, despite the use of metal chlorides as precursors. The titanium to vanadium metal ratio could, however, be reliably obtained from the electron probe spectra and, in Figure 3, these values are plotted for each of the measured positions on the substrate. This supports the results found from the diffraction analysis, showing a compositional range, with each spot having a differing Ti/V ratio, following the same trend as the changing a lattice parameter. This follows a Vegard's law relationship which can be seen by a plot of lattice parameter against the Ti/V content for the twelve alloy points, as is shown in Figure 4. Thus our results show that the relationship between the lattice parameter and the composition for a member of the $Ti_xV_{1-x}N$ solid solution can be approximated as $a = 0.13x + 4.10$, where a is the lattice parameter and x is the metal ratio factor in $Ti_xV_{1-x}N$.

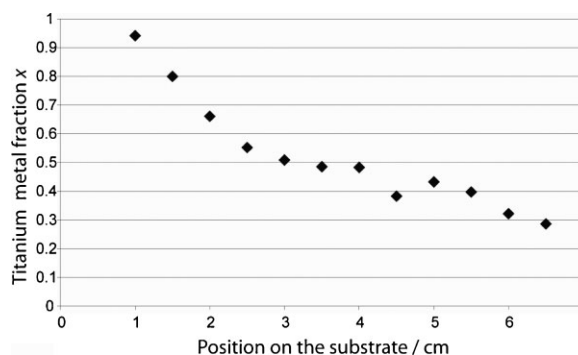


Fig. 3. The titanium metal fraction x in $Ti_xV_{1-x}N$ as determined by electron probe plotted as a function of position on the substrate.

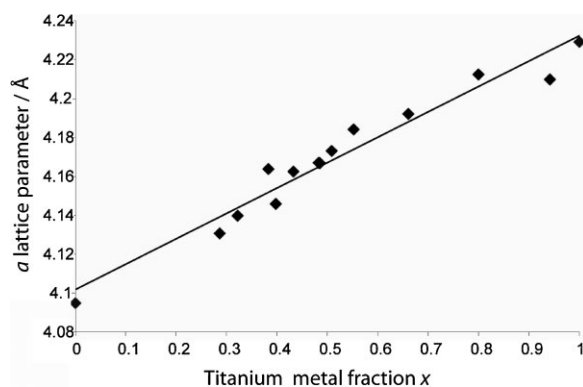


Fig. 4. Lattice parameter of the spots determined from XRD plotted against the fraction of titanium x in $\text{Ti}_x\text{V}_{1-x}\text{N}$ as determined by electron probe. Additionally, the lattice parameters of TiN and VN are also plotted (in red).

The optical reflection and transmission of the spots were recorded to assess the effectiveness of the films as heat mirrors. As an ideal heat mirror has a strong reflection in the IR, combined with high visible transmittance, an effective measure of the suitability of a film for solar control can be derived by multiplying the maximum visible transmittance by the reflectance at 2000 nm, this gives a figure of merit, $T_{(\text{max})}R_{(2\ \mu\text{m})}$, that can be used to compare different films.^[19] The value is most effective when comparing films of similar thickness, as the transmittance and reflectance vary in a nonlinear fashion with thickness.^[21] The thickness of the different spots was determined using side-on SEM and found to vary from 0.93 to 4.15 μm , a range too great to allow effective comparison of the direct figure of merit values. However the reflectance and transmittance values can be normalized, as the relationship between transmittance and thickness is given by the Beer-Lambert law, and it has been found experimentally for TiN that the reflectance, R , varies with thickness according to $e^R = 1 + \alpha L$, where L is the path length or thickness, and α is a constant.^[21] Using these relationships, the transmittance and reflectance values for all twelve spots of $\text{Ti}_x\text{V}_{1-x}\text{N}$ were normalized to the values expected for films of 500 nm thickness, and the $T_{(\text{max})}R_{(2\ \mu\text{m})}$ calculated. These values are plotted in Figure 5, along with values taken from films of pure TiN and VN for comparative purposes. This shows that TiN is more effective than VN as a heat mirror at this film thickness, but also that any extent of mixing decreases the effectiveness of the pure compounds as heat mirrors, dramatically so for TiN, with the worst figure of merit being found in $\text{Ti}_{0.5}\text{V}_{0.5}\text{N}$ with $T_{(\text{max})}R_{(2\ \mu\text{m})} = 0.04$ compared with the highest value of 0.20 found in pure TiN.

3. Conclusions

The results discussed above have shown that it is indeed possible to generate a compositional spread of the solid solution $\text{Ti}_x\text{V}_{1-x}\text{N}$ by the use of a combinatorial APCVD

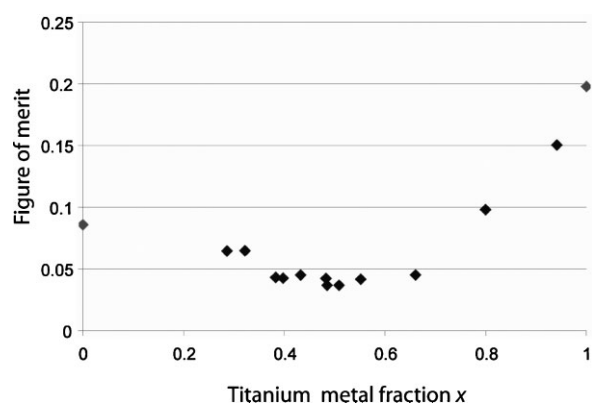


Fig. 5. Plot of the $T_{(\text{max})}R_{(2\ \mu\text{m})}$ normalized to 500 nm film thickness against composition for the various values of $\text{Ti}_x\text{V}_{1-x}\text{N}$. Values for the pure end member compounds are also given, shown in red.

synthetic method, in which a large number of distinct compositions of the solution (in this case twelve distinct phases) can be observed and investigated individually. In other words, by using a combinatorial method it has been possible, using a single synthetic step, to replicate the results of at least twelve separate experiments that would have been needed to generate the same result with standard APCVD methodology.

4. Experimental

Synthesis: Using a cold-wall APCVD reactor, deposition of the $\text{Ti}_x\text{V}_{1-x}\text{N}$ film onto glass substrates 200 mm \times 90 mm \times 3 mm, in length, width, and thickness, was carried out. The glass substrates were heated in the reactor by being placed on a graphite block containing three Whatman heater cartridges. All inlet lines were heated to 150 $^\circ\text{C}$ to prevent the precursors from condensing before they entered the reactor.

The precursors used to generate the film were TiCl_4 , VCl_4 , and NH_3 . The metal chlorides were heated in bubblers and transported to the reactor using a carrier gas of N_2 , and further diluted with plain flows of N_2 gas before entering the baffle manifolds at the front of the reactor. NH_3 was transported using its room temperature vapor pressure. In a standard APCVD reactor, all of the reagent gases are combined in a single mixing chamber and then passed through a series of baffles to produce a laminar gas flow in the reactor. In order to produce the compositional spread required for the combinatorial work, an asymmetry has to be introduced to the film. This was achieved by using a modified baffle manifold with three reagent entry points to produce three parallel linear gas streams which could not mix until they entered the reactor. Overall the reactor inlet was 94 mm wide and each of the three separate baffle inlets was 24 mm wide, with 11 mm separators between the central manifold entry and the two outer manifold entry points. Each of the three precursors entered separately through one of these manifold streams. The distance from the front of the manifold to the front edge of the substrate was 50 mm. Lateral diffusion of each of the reagents then produced the overlap in composition to produce the combinatorial distribution. The diffusion of the metal chlorides was found to be somewhat limited so they were placed in adjacent gas streams, with VCl_4 entering through the middle baffle, and TiCl_4 through the right hand baffle, orientated relative to the direction of gas flow. This proximity produced an overlap region of titanium and vanadium precursors of 70 mm at its widest point, 90 mm in from the leading edge of the film, perpendicular to the gas flow. The much lighter NH_3 molecule was found to have a much higher diffusion rate, as predicted by kinetic theory, and was therefore injected through the left hand baffle and was sufficiently mobile to pass across and provide a nitrogen source for film deposition across the whole substrate. A diagram showing the layout of the apparatus is given in Figure 6.

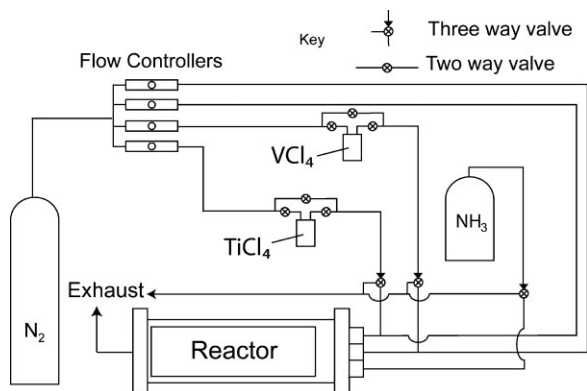


Fig. 6. Schematic diagram of the CVD apparatus, with multiple entry points to allow asymmetric depositions.

For the film used in this combinatorial study, deposition was carried out with a substrate temperature of 630 °C for 30 s. This temperature was chosen to maximize the crystallinity of the film, at the maximum temperature to which the glass could be heated without softening. The TiCl₄ bubbler was heated to 73 °C, and vapor transported with 0.75 L min⁻¹ of N₂ and combined with a plain flow of 5.25 L min⁻¹. The VCl₄ was heated to 29 °C, transported with 2 L min⁻¹ and diluted in 4 L min⁻¹ of N₂ gas. The ammonia gas was supplied at a flow rate of 0.13 L min⁻¹, using the room temperature vapor pressure of the gas. These parameters are equivalent to molar flows of 1.1 × 10⁻³ mol min⁻¹ of VCl₄, 5.1 × 10⁻³ mol min⁻¹ of TiCl₄, and 5.3 × 10⁻³ mol min⁻¹ of NH₃. Despite the TiCl₄ molar flow being approximately five times that of VCl₄, the ratio of metals deposited into the film varied with position in such a way as to be more consistent, with approximately equivalent deposition rates (Fig. 3). This would suggest a significant difference in the reactivity of the two metal chlorides.

XRD Analysis: Powder XRD analysis of the film was conducted using a Bruker D8 GADDS diffractometer. This was equipped with a micro-focused Cu K α X-ray source, Göbel mirror collimation, a 2D area X-ray detector, and a motorized sample stage. This set-up allowed diffraction patterns of several small discrete spots of the substrate to be recorded rapidly and automatically in sequence. This allows the composition of the surface to be mapped – the efficacy of this procedure has been reported previously [13]. To analyze the compositional spreads made in the film, patterns were recorded in a line perpendicular to the direction of reagent flow and 90 mm in from the leading edge of the film, on spots separated by 5 mm. This allowed a total of sixteen spots to be recorded across the 90 mm-wide substrates. Patterns were analyzed using Rietveld analysis with the GSAS package and the EXPGUI interface [24, 25].

Elemental Analysis: The titanium to vanadium ratio of the samples was determined using a Jeol JXA-8100 superprobe SEM electron probe.

Spectroscopy: The absorption and reflection of the film was recorded in the range 300–2500 nm, covering the near-UV to far-IR of the electromagnetic spectrum, using a Perkin Elmer λ 950 photospectrometer.

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