The Use of Combinatorial Chemical Vapor Deposition in the Synthesis of Ti$_{3-\delta}$O$_4$N with 0.06 $<$ $\delta$ $<$ 0.25: A Titanium Oxynitride Phase Isostructural to Anosovite

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Abstract: We employ, for the first time, a unique combinatorial chemical vapor deposition (CVD) technique to isolate a previously unreported transition-metal mixed-anion phase. The new oxynitride phase, Ti$_{3-\delta}$O$_4$N (where 0.06 $<$ $\delta$ $<$ 0.25), is the first example of a complex titanium oxynitride and was synthesized within composition graduated films formed from atmospheric pressure CVD of TiCl$_4$, NH$_3$, and ethyl acetate. Characterization was performed by X-ray diffraction, X-ray photoelectron spectroscopy, UV-visible spectra, and SQUID magnetometry. The material crystallizes in the $Cmcm$ space group, with the ordered nitrogen ions stabilizing the orthorhombic analogue of the monoclinic anosovite structure, $\beta$-TiO$_2$N. The lattice parameters are sensitive to composition, but were determined to be $a = 3.8040(1)$ Å, $b = 9.6486(6)$ Å, and $c = 9.8688(5)$ Å for Ti$_{2.852}$O$_4$N. Powder samples were prepared through delamination of the thin films for synchrotron X-ray diffraction and magnetic measurements. It is the first example of a new phase to be synthesized using such a combinatorial CVD approach and clearly demonstrates how such techniques can provide access to new materials. This metastable phase with unusual nitrogen geometry has proved to be elusive to conventional solid-state chemistry techniques and highlights the value of the surface growth mechanism present in CVD. Furthermore, the ease and speed of the synthesis technique, combined with rapid routes to characterization, allow for large areas of phase space to be probed effectively. These results may have major implications in the search for new complex mixed-anion phases in the future.

The tendency of nitrides to decompose more readily than oxides as well as to oxidize under atmospheric conditions has historically made synthesis of new nitrides far more difficult than oxides, and consequently they have received much less attention. Despite this relative neglect, nitride phases constitute a significant number of technologically important materials, for example GaInN in blue lasers and LEDs. The relatively high occurrence of useful nitride materials has inspired researchers more recently to refocus on complex ternary and quaternary nitride and oxynitride phases. Among these nitrides, there has been particular interest in titanium containing phases, motivated by their importance and wide use as wear resistant and solar control coatings, barrier layers in silicon electronics, and in the case of titanium nitride as a decorative gold-colored coating.

Previous investigations into titanium oxynitrides have uncovered a series of cubic titanium compounds with the rock salt structure and empirical formula TiO$_x$N$_y$ where the sum of $x$ and $y$ is approximately 1. Materials where the sum of $x$ and $y$ is significantly different to 1 have also been reported. However, in all cases the compound maintains the rock salt structure and accommodates the nonstoichiometry through vacancies on the sublattice sites. These TiO$_x$N$_y$ phases can be considered as a solid solution of titanium(III) nitride, TiN, and the cubic titanium(II) oxide, TiO, with the cubic lattice parameter $a$ of a given TiO$_x$N$_y$ being found by a Vegard’s Law relationship between the value of $a = 4.244$ Å for TiN and $a = 4.172$ Å for TiO. A second type of titanium oxynitride has been extensively reported: the doping of TiO$_2$ with nitrogen. Research on these materials has been conducted principally to change the band gap of titania and alter its hydrophilic and photocatalytic properties. The extent of this doping is extremely small however, typically less than 0.5 atom % of nitrogen, and

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as such are best considered as nitrogen doped materials rather than as true titanium oxynitrides.14–16

In contrast to the close-packed cubic TiO₂ materials (d ≈ 5.8 g/cm³) the new titanium oxynitride presented here is based on nitrogen substitution into the less dense (d ≈ 4.3 g/cm³) orthorhombic α-Ti₃O₅ structure, representing what we believe is the first time that anionic substitution has been shown to occur in this material.

The mineral Anosovite was first identified as magnesium-doped Ti₃O₅, an orthorhombic pseudo-brookite phase with lattice parameters a = 3.747 Å, b = 9.465 Å, and c = 9.715 Å, by Rusakov and Zhdanov in 1951.17 Pure single-crystal studies of Ti₃O₅ have found that at room temperature the structure is actually a related monoclinic cell with lattice parameters a = 9.752 Å, b = 3.802 Å, c = 9.442 Å, and β = 91.55°,18 which is known as β-Ti₃O₅. On being heated above room temperature β-Ti₃O₅ undergoes a phase transition between 450 and 460 K (depending on the direction of the transition) to a high-temperature monoclinic phase (β′) followed by a further transition above 500 K to the orthorhombic Anosovite structure proposed by Rusakov and Zhdanov,19 referred to as α-Ti₃O₅. Additionally two more structures are known to be present in the phase diagram below room temperature, known as γ and δ.20

The room-temperature monoclinic β-Ti₃O₅ is a semiconductor in which there are three distinct crystallographic titanium sites, each at the center of a distorted TiO₂ octahedron but with evidence of electron localization and metal–metal bonding, similar to the Verwey transition first identified in Fe₃O₄.21 Bond valence calculations derive valences of these sites as +3, +3½, and +3½.18 The localization of the electron density onto the d¹Ti¹⁺ ions allows metal–metal bonds to form between them, such that the Ti¹⁺ ions form “dimers” within the structure with a bond distance of 2.61 Å. The other two crystallographic sites also form a closely associated metal–metal group, a zigzag tetramer of the form Ti³⁻(Ti⁻)³⁻(Ti⁺)³⁻(Ti⁺)³⁻ with metal–metal distances of 2.82 Å, 2.77 Å, and 2.82 Å.18,22 Each group of four titanium ions has two delocalized electrons, which may contribute to a degree of metal–metal bonding within the tetramer.18 The transformation to the high-temperature α-Ti₃O₅ removes this inequivalency, disrupts the metal–metal bonds, and delocalizes the electrons formerly used in this bonding. The number of distinct titanium crystallographic sites is reduced to two, and metallic behavior is observed showing that the electrons, no longer used for direct metal–metal bonds, become fully delocalized.22 Bond valence calculations also derive the expected average value of +3½ for both sites,18 and the shortest Ti–Ti distance increases from 2.61 Å, found in β-Ti₃O₅, to 2.89 Å.

It has been found that cationic substitution into Ti₃O₅ with small amounts of metal ions (as little as 3–6% of the metal

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in heated bubblers, then transported to the mixing chamber by N$_2$ (BOC, Aldrich 99.9%) and ethyl acetate (BDH, GPR grade) were volatized to approximately 1000 products. A schematic diagram of the apparatus is given in Figure 1.

Previous atmospheric pressure CVD work has successfully synthesized TiN phases from TiCl$_4$ and NH$_3$. In the work presented here, the Ti–O–N system was formed by addition of ethyl acetate as an oxygen source. In the previous work on titanium nitride it was found that TiCl$_4$ and NH$_3$ react rapidly in the gas phase to form solid adducts, these can be detrimental to deposition and cause blockages if the vapors are combined too early. The problem of blockage was avoided in this work by introducing TiCl$_4$ and NH$_3$ into the reactor separately, one through each of the two mixing chambers. The third reagent, ethyl acetate, was introduced through the same mixing chamber as TiCl$_4$; so one mixing chamber (the right-hand one) introduced the TiCl$_4$ and ethyl acetate reagents, and the other mixing chamber (the left-hand one) introduced NH$_3$ to the reactor. TiCl$_4$ (Aldrich 99.9%) and ethyl acetate (BDH, GPR grade) were volatized in heated bubblers, then transported to the mixing chamber by N$_2$ (BOC, oxygen free) carrier gas where the TiCl$_4$ and ethyl acetate streams were combined with each other and a plain line of N$_2$ as makeup gas. NH$_3$ (BOC, anhydrous) was transported under its own vapor pressure and also combined in the left-hand mixing chamber with a plain line of N$_2$. This produced the conditions for the combinatorial aspect of this work, as the oxygen and nitrogen sources entered from opposite sides of the reactor, creating a gradient in the O:N ratio present in the precursor mix horizontally across the substrate and thus a range of deposition conditions in a single experiment.

The use of three precursors provided us with a large number of experimental parameters: temperature, NH$_3$ flow rate, ethyl acetate flow rate, and TiCl$_4$ flow rate among others; so for simplicity, in the work presented here, the ethyl acetate (oxygen source) flow rate was set such that the ethyl acetate flow rate varied from 0 to 0.0196 mol min$^{-1}$. The TiCl$_4$ and NH$_3$ flow rates used were kept at approximately 0.1 mol min$^{-1}$, while the oxygen source (ethyl acetate) flow rate was varied from 0 to 0.0196 mol min$^{-1}$. Film synthesis was carried out using a deposition time of 300–2500 nm.

X-ray photoelectron spectroscopy was conducted using an Escalab 220i-XL instrument with Al K$_\alpha$ radiation. Survey scans were recorded in the range 0–1100 eV (binding energy), and then smaller range, higher resolution scans were recorded of the principal peaks of Ti (2p), O (1s), N (1s), C (1s), and Si (2p). The peaks were modeled using the CasaXPS software system to determine their area, adjusted using sensitivity factors, thus allowing the film composition to be calculated.

The recorded diffraction data were modeled using either Le Bail fitting or Rietveld Refinement, both carried out using the GSAS software suite.

UV–visible transmission and reflection spectroscopy was conducted using a Helios double beam instrument built for compatibility with samples of thin-films on glass substrates. Measurements were standardized relative to a rhodium mirror (reflectance) and blank glass slides (transmission). Absorption, transmission, and reflection spectra were recorded in the range 300–2500 nm.

The film covered the whole of the substrate but was divided into two sections of different color in transmission: one brown and the other green. The division between these two

Figure 1. Schematic diagram of the APCVD apparatus, with top down view of the reactor. Of particular importance are the two mixing chambers, with two separate entry points to the reactor, mixing chamber A (on the right) and mixing chamber B (on the left). Left and right in this context are orientated with the forward direction being through the reactor toward the exhaust.

Results and Discussion

Films of Ti$_3$–$\alpha$O$_4$N were successfully synthesized from TiCl$_4$, ethyl acetate, and NH$_3$ precursors. All of the reactant flow parameters were kept constant between experiments, except for the ethyl acetate flow rate which was varied to alter the oxygen to nitrogen precursor ratio. In the two films considered in detail here, the ethyl acetate (oxygen source) flow rate was set such that the N:O ratio in the respective precursors was either 2:1 or 1:1.

Film Formed Using Nitrogen to Oxygen Precursor Ratio of 2:1. The film covered the whole of the substrate but was divided into two sections of different color in transmission: one brown and the other green. The division between these two

sections ran diagonally across the substrate such that each colored section was approximately a right angled triangle, with the brown section having its base along the inlet-edge, nearest to the NH3 inlet. A photograph of this is shown in Figure 2. All of the films produced were adhesive and stable in air with time.

The colors of the two sections of the film were confirmed by UV−vis spectroscopy, whereby two areas of each of the colored sections of the film were analyzed (these spectra can be seen in the supplementary data). All the spectra show a single very broad asymmetric peak, with a sharp rise at the shorter wavelengths, peaking, and then a trailing edge running into the longer wavelengths. Significantly the spectra taken from spots of the green and brown sections were converted into the L.a.b. color coordinate system38 which found that in transmission the green section has a,b coordinates of −24.4, 26.43 and the brown section has coordinates of −1.93, 76.75.

The side on SEM measurements conducted on a range of spots in both the green and brown colored sections found that the film thickness was reasonably consistent across the substrate measured as 1300 nm in the green section, and 1000 nm in the brown section, for this deposition of 1 min. The top-down SEM images revealed a similarly consistent morphology for both colored sections of the film, reminiscent of fused platelets. Figure 3 shows an example SEM image of the film morphology.

To determine the composition of the film XPS analysis was conducted on two sections of the film, one from the brown section and one from the green section (Table 2). Peak positions were calibrated relative to an adventitious trace surface carbon impurity taken to be at 284.6 eV. This found that both sections of the film contained Ti, O, and N. In the brown section of the film the O 1s peak was found at 530.1 eV and the N 1s at 395.9 eV, values consistent with the database values for O2− and N3−. The peak positions for Ti 2p3/2 (eV) O 1s (eV) N 1s (eV) are also given, for comparison.

The values found in TiO2, TiN, and TiO2N, are also given, for comparison.

Table 1. Details of Reaction Conditions Used to Form Films to Investigate the Ti−O−N System

<table>
<thead>
<tr>
<th>TiCl4 molar flow</th>
<th>NH3 molar flow</th>
<th>ethyl acetate bubbler temp</th>
<th>ethyl acetate carrier gas flow</th>
<th>ethyl acetate flow rate</th>
<th>composition of the film</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol min⁻¹</td>
<td>mol min⁻¹</td>
<td>K</td>
<td>L min⁻¹</td>
<td>mol min⁻¹</td>
<td></td>
</tr>
<tr>
<td>0.012</td>
<td>0.018</td>
<td>N/A</td>
<td>0</td>
<td>0</td>
<td>TiN</td>
</tr>
<tr>
<td>0.012</td>
<td>0.018</td>
<td>29</td>
<td>0.2</td>
<td>0.0015</td>
<td>TiN and Ti1−xOxN</td>
</tr>
<tr>
<td>0.012</td>
<td>0.018</td>
<td>34</td>
<td>0.5</td>
<td>0.0048</td>
<td>Ti1−xO2N</td>
</tr>
<tr>
<td>0.012</td>
<td>0.018</td>
<td>30</td>
<td>1.0</td>
<td>0.0078</td>
<td>Ti1−xO2N</td>
</tr>
<tr>
<td>0.012</td>
<td>0.018</td>
<td>30</td>
<td>2.5</td>
<td>0.0196</td>
<td>TiO2 and Ti1−xO2N</td>
</tr>
</tbody>
</table>

Table 2. Values for the Binding Energies of the Ti 2p3/2, O 1s, and N 1s Peaks Found in the X-ray Photoelectron Spectra of the Green and Brown Sections of the First Film, with an N:O Precursor Ratio of 2:1<sup>a</sup>

<table>
<thead>
<tr>
<th>compound</th>
<th>peak position in binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti 2p3/2 (eV)</td>
</tr>
<tr>
<td>brown section of film</td>
<td>458.0</td>
</tr>
<tr>
<td>TiO2</td>
<td>458.6</td>
</tr>
<tr>
<td>TiN</td>
<td>455.1</td>
</tr>
<tr>
<td>TiO2N&lt;sub&gt;x&lt;/sub&gt;</td>
<td>456.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> The values found in TiO2, TiN, and TiO2N, are also given, for comparison.

Figure 2. Photograph of the film formed using 0.0048 mol min⁻¹ of ethyl acetate, showing the two colored regions, one green and one brown.

Figure 3. SEM image showing the unusual “fused platelet” morphology found in all of the films of Ti1−xO2N.
Vapor Deposition in the Synthesis of Ti<sub>3</sub>-xO<sub>y</sub>N

The results of the diffraction strongly suggest that a new phase has been synthesized, with a structure analogous to high-temperature orthorhombic $\alpha$-Ti<sub>3</sub>O<sub>5</sub> ($\text{TiO}_{1.67}$), but with nitrogen insertion, as determined by the presence of nitrogen peaks in the XPS, with a binding energy associated with titanium nitrides and oxynitrides and the change in lattice parameters observed from the indexing of the diffraction patterns. The XPS compositional results gave anion/metal ratios of 1.70 and 1.78 for the brown and green sections, respectively, compared to the expected 1.67 based on this Ti<sub>3</sub>X<sub>5</sub> model, so there is an excess of anions. This can be interpreted as extra-anion intercalation with a fully occupied metal sublattice, or as a normally occupied anionic sublattice, with vacancies on the metal sublattice accounting for the higher ratio. The lack of suitable sites in the structure for anion intercalation, and indeed further evidence from X-ray diffraction (that will be discussed later, in regard to the powder samples of oxy-nitride), effectively precluded the occupation of intercalation sites. Such titanium sublattice vacancies have previously been observed in cationic-doped Mg<sub>0.2</sub>Ti<sub>2.6</sub>O<sub>5</sub> and also in the nitride Ti<sub>0.76</sub>N, so it is reasonable to suggest that a similar titanium deficiency occurs in Ti<sub>3</sub>-xO<sub>y</sub>N. This yields a formula of Ti<sub>2.94</sub>O<sub>1.96</sub>N<sub>1.00</sub> for the brown section and Ti<sub>3.85</sub>O<sub>4.34</sub>N<sub>1.60</sub> for the green section, with O/N ratios of 4:1 in both sections. The variation in titanium content gives the two different sections different titanium oxidation states of +3.7 for the brown section and of +3.9 for the green section. These values are above the threshold oxidation state of +3.47 for stability of the monoclinic Ti<sub>3</sub>O<sub>5</sub> structure and explain why the orthorhombic structure is observed.

The sheet conductivity of the films was measured, and the experiments found that the green sections of film had sheet resistivity of 300–500 ohms/square, while the brown sections had values of 5000–6000 ohms/square. This is a significant difference in the sheet resistance between the two sections, which may be due to fundamental differences in conductivity between them, but sheet resistance is not simply dependent on the electronic properties of the material but also heavily influenced by such factors as film thickness and surface morphology. Given the similarities in structure and oxidation state, as implied from the diffraction and XPS measurements, it seems likely that the increased thickness of the green section (1300 nm vs 1000 nm) leads to a relative reduction in its resistance. Differences in morphology may also be playing a critical role.

**Film Formed Using a Nitrogen to Oxygen Precursor Ratio of 1:1.** In a second set of films the ethyl acetate reactant flow was increased to 0.0078 mol min<sup>-1</sup>, while the NH<sub>3</sub> and TiCl<sub>4</sub> flow rates were maintained at the same levels as in the previous film, thus giving a O:N precursor ratio of 1:1. Visual inspection of the film formed under these conditions found that it was green in color across the whole substrate, with no brown section. A UV–vis spectrum recorded on this film shows that it was identical to that recorded on the green section of the first film. Side-on SEM imaging again gave a thickness of 1300 nm, grown in 1 min.

The X-ray diffraction pattern recorded on the film synthesized with the higher ethyl acetate content could also be indexed using a similar cell as the patterns recorded on the two-colored film; a Le Bail fitting in the $Cmcm$ space group gave lattice parameters of $a = 3.781(1)$ Å, $b = 9.697(1)$ Å, and $c = 9.901(1)$ Å, with a unit cell volume of 363.1(1) Å<sup>3</sup>.

Because of these limitations Le Bail fitting<sup>13</sup> was used to determine the lattice parameters that best fitted the observed diffraction peaks, conducted in the $Cmcm$ space group of Anosovite. This refinement found that the parameters of the green section were $a = 3.781(1)$ Å, $b = 9.697(1)$ Å, and $c = 9.901(1)$ Å, with a unit cell volume of 363.1(1) Å<sup>3</sup>.

These cell volumes compare to 350 Å<sup>3</sup> found in the pure monoclinic Ti<sub>3</sub>O<sub>5</sub>. Similarly high unit cell volume values of 365–370 Å<sup>3</sup> are, however, found in the cationically substituted Mg<sub>0.2</sub>Ti<sub>2.6</sub>O<sub>5</sub> ($0.3 < x < 0.9$)<sup>27</sup> and Li,Ti<sub>3</sub>O<sub>5</sub> ($0.05 < x < 0.5$).<sup>23</sup>

Inadvertent metal doping, however, cannot explain the properties observed in the films prepared in this work as the XPS and WDX study has revealed that no metal ions other than titanium are present, within the 0.1 atom % detection limit, in the necessary amounts (ca. 7 atom %) to stabilize the orthorhombic phase.

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The XPS analysis conducted on this second film gave the composition, assuming anionic substitution, as Ti$_{2.75}$O$_{4.10}$N$_{0.90}$ (35.4 atom % Ti, 53.0 atom % O, and 11.6 atom % N), with an O/N ratio of 4.58. This composition has a slightly higher O:N ratio than the green section of the previously discussed film, as would be expected given the change in precursor ratio, but this change in O:N ratio does not seem to have a significant effect on either the lattice parameters or the UV–vis spectroscopic properties. Instead the film color seems to be dependent on the oxidation state of the titanium ion, which in the green sections lies between +3.91 and +3.96, while the brown section of the first film has a lower oxidation state of +3.7. The XPS results from all the analyzed sections of both films are summarized in Table 3.

### Analysis of the Powder Sample
In terms of the materials structure, the recurrent problem in both of the discussed films was that effective structural refinement could not be carried out using the diffraction data recorded on them, owing to the presence of a large degree of preferred orientation. This problem was overcome by a further experiment using the higher ethyl acetate precursor conditions (0.0078 mol min$^{-1}$), which confirmed that these conditions were able to overcome the presence of a large degree of preferred orientation. This problem was also observed in the pattern of this second film preventing structural refinement being conducted.

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### Analysis of the Powder Sample
In terms of the materials structure, the recurrent problem in both of the discussed films was that effective structural refinement could not be carried out using the diffraction data recorded on them, owing to the presence of a large degree of preferred orientation. This problem was overcome by a further experiment using the higher ethyl acetate precursor conditions (0.0078 mol min$^{-1}$), which confirmed that these conditions were able to overcome the presence of a large degree of preferred orientation. This problem was also observed in the pattern of this second film preventing structural refinement being conducted.

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a unit cell volume of 349.7 Å³. The expansion of the unit cell caused by the nitrogen doping cannot be explained on the basis of changes in the titanium–anion bond length, as the average bond length in both β-Ti₃O₅ and Ti₂.85(2)O₄N is 2.02(1) Å. Instead the principle reason for the expansion is the breaking of the titanium–titanium bonds present in β-Ti₃O₅, where the shortest metal–metal distance is 2.61 Å. In Ti₂.85(2)O₄N the shortest metal–metal distance has been increased to 2.99 Å; the presence of nitrogen increases the formal oxidation state of the Ti to near +3.86, above the threshold of +3.47 where the metal–metal bonding that stabilizes the monoclinic form is disrupted. Comparison with the Li⁺ and Mg²⁺ metal-doped TiO₂ shows that the sample has an extremely small susceptibility, consistent with the small number of d-electrons available per Ti. Examination of the magnetization against field measurements found that the response was linear above 1.5 T (where small ferromagnetic impurities had been saturated). The variation in the magnetic susceptibility with temperature was found by taking the gradient of the magnetization between measuring fields of 3 T and 4 T and is plotted in Figure 8. This shows that the sample has an extremely small susceptibility, consistent with the small number of d-electrons available per titanium ion (0.14 e⁻/Ti), and no features in the variation of temperature indicative of either ferromagnetic or antiferromagnetic behavior. A plot of the inverse susceptibility against temperature gives a nonlinear plot (also Figure 8), showing that in this temperature range the material is not in the Curie–Weiss regime.

It is interesting to note that over 1000 papers have been published on the cubic titanium oxynitride, over 300 on the

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**Table 4. Structural Parameters of the Ti₂.85O₄N Model**

<table>
<thead>
<tr>
<th>atom site</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso (Å²)</th>
<th>fractional occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>4c</td>
<td>0.6956(2)</td>
<td>0.25</td>
<td>0.001</td>
<td>0.923(6)</td>
<td></td>
</tr>
<tr>
<td>Ti2</td>
<td>8f</td>
<td>0.6392(1)</td>
<td>0.5663(1)</td>
<td>0.001</td>
<td>0.958(5)</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>8f</td>
<td>0.1861(4)</td>
<td>0.5715(4)</td>
<td>0.005(1)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>8f</td>
<td>0.5470(5)</td>
<td>0.3825(3)</td>
<td>0.005(1)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>N3</td>
<td>4c</td>
<td>0.7341(6)</td>
<td>0.75</td>
<td>0.005(1)</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

* Cmcm space group with a = 3.8040(1) Å, b = 9.6486(6) Å, c = 9.8688(5) Å and volume = 362.21(2) Å³; χ² = 0.9454, wR = 3.21%, and R = 3.9% for 49 variables recorded at 295 K.

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**Table 5. Ti–O and Ti–N Bond Lengths for Each of the Titanium Environments Found in the Structure of Ti₂.85O₄N**

<table>
<thead>
<tr>
<th>Ti1 environment</th>
<th>bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1–O1 (x2)</td>
<td>1.9567(9)</td>
</tr>
<tr>
<td>Ti1–O1</td>
<td>2.159(4)</td>
</tr>
<tr>
<td>Ti1–O2</td>
<td>2.026(4)</td>
</tr>
<tr>
<td>Ti1–O2</td>
<td>1.861(4)</td>
</tr>
<tr>
<td>Ti1 – N3</td>
<td>2.026(9)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ti2 environment</th>
<th>bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti2–O1 (x2)</td>
<td>2.095(4)</td>
</tr>
<tr>
<td>Ti2–O2 (x2)</td>
<td>1.947(5)</td>
</tr>
<tr>
<td>Ti2–N3 (x2)</td>
<td>2.021(2)</td>
</tr>
</tbody>
</table>

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**Figure 6.** Representation of the unit cell of the Ti₂.85O₄N model. Grey atoms are titanium, red are oxygen, and blue is nitrogen: (a) view of the 001 face; (b) view of the 100 face.

**Figure 7.** Representation of the coordination environment of the ions in the structure, with bond lengths marked in Å: (a) Ti2, (b) Ti1, (c) O1, (d) O2, (e) N3.

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**Figure 8.** Vapor Deposition in the Synthesis of Ti₂.85O₄N.
nitrogen doping of TiO₂ (based on a search of the chemical abstracts of titanium oxynitride and nitrogen-doped TiO₂, respectively). So the titanium–oxygen–nitrogen system is one that has been extensively investigated over a number of years. So the appearance of a previously unreported, room-temperature phase, with a structure significantly different to any currently reported titanium oxynitride is an unexpected result given this intensive scrutiny. The reason for its discovery in this work is the use of combinatorial chemical vapor deposition. CVD provides a radically different reaction pathway compared to traditional solid-state techniques, and the combinatorial aspect involved allows a large number of conditions to be trialed simultaneously. This work, then, highlights the advantages that both a combinatorial approach and the use of nontraditional synthetic methods can present to materials research.

Conclusions

In this paper a new ternary oxynitride, Ti₁₂₋₅O₄N, with a range of titanium ion vacancy δ = 0.06–0.27 has been described. The chemical composition was confirmed by XPS analysis and the structure of the δ = 0.15 phase, Ti₁₂₋₅O₄N, was determined from Rietveld refinement against powder X-ray diffraction data recorded using a synchrotron source. The compound was made using a combinatorial approach to CVD and shows how this approach may be a fruitful method for new phase synthesis. The novel oxynitride is isostructural to the high-temperature phase of Ti₃O₅, a preference for this Cmcm structure at room temperature similar to that frequently observed by cationic doping of Ti₃O₅, and caused in both cases by the removal of titanium d-electrons that are used in the room-temperature undoped Ti₃O₅ to form the metal–metal bonds that stabilize the monoclinic structure. The structural analysis of Ti₁₂₋₅O₄N shows that the nitrogen present substitutes for oxygen on a single crystallographic 4c site. To our knowledge this is the first time that anionic doping has been carried out in the Ti₃O₅ structure and provides an interesting comparison to the extensive cationic doping studies carried out on the structure. Previous to this study the only binary titanium oxides known to incorporate nitrogen to form an oxynitride was the rock-salt TiO, and the very low levels of inclusion found in nitrogen-doped titania. This discovery of Ti₁₂₋₅O₄N based on Ti₃O₅ opens up the possibility of forming many oxynitrides based on the range of binary oxides known for titanium.

Acknowledgment. The EPSRC is thanked for funding. Pilkington Group Limited is thanked for supplying glass substrates. For assistance with spectroscopic measurements we would like to thank Dr. Russell Binions, and for help with SEM measurements we thank Mr. Kevin Reeve. Dr. Larry Margulies, ESRF, is especially thanked for his generous assistance and efforts with the diffraction experiments. I.P.P. is a Wolfson/Royal Society merit award holder.

Supporting Information Available: UV–visible transmission spectra of the different colored sections of the films discussed; a full list of bond angles from the Rietveld refinement of Ti₁₂₋₅O₄N. This material is available free of charge via the Internet at http://pubs.acs.org.

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