

A Facile Route to Thin Films of Zinc Carbodiimide using Aerosol Assisted Chemical Vapor Deposition

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KEYWORDS: Chemical Vapor Deposition, Thin Film, Zinc Cyanamide, Zinc Carbodiimide,
Aerosol Assisted

ABSTRACT

There has been a resurgence of interest in metal carbodiimides in recent years and in this paper we will present a route to the synthesis of one of these phases, zinc carbodiimide, previously known as zinc cyanamide, in the form of a sub-micron thin film. This was achieved using aerosol assisted chemical vapor deposition from a solution of zinc acetate and urea in methanol, with the carbodiimide ion being formed from the decomposition of the urea molecule. Thin film synthesis was achieved over a deposition temperature range of 375 °C to 500 °C, with a minimum ratio of urea to zinc acetate of 2:1 and a maximum of 5:1 established as viable for film formation. The presence of zinc carbodiimide was confirmed using energy dispersive X-ray analysis, infra-red spectroscopy and powder X-ray diffraction, where it was found to crystallize in the $I\bar{4}2d$ space group with lattice parameters $a = 8.777 \text{ \AA}$ and $c = 5.407 \text{ \AA}$. This work represents the first example of the synthesis of a ZnNCN thin film, or indeed any metal carbodiimide thin film, using a chemical vapor deposition technique.

Introduction

In this paper we will present a facile route to thin films of zinc carbodiimide using the aerosol assisted chemical vapor deposition (AACVD) of zinc acetate and urea in methanol solution. The synthesis of bulk powder zinc carbodiimide, historically but now incorrectly referred to as zinc cyanamide, has been possible since the early 20th century with the first report in 1931 of the action of cyanogen on zinc oxide.^[1] It has subsequently been synthesized using the reaction of cyanamide, H₂NCN, with hydrated zinc oxide slurry,^[2] and *via* a salt metathesis reaction of sodium cyanamide and zinc sulfate.^[3] In a process to which our thin film synthesis is more analogous, bulk zinc carbodiimide has also been made by the reaction of zinc oxide with three equivalents of urea at 135 °C, followed by calcination at 600 °C.^[4] However, no previous work has identified a route to the formation of a thin film of the material.

Zinc carbodiimide has a wide indirect band gap of 4.32 eV, which can be compared with 3.3 eV for zinc oxide.^[5] Applications of zinc carbodiimide are based around its ability to act as an anti-stain, anti-corrosive, and anti-fungal pigment additive,^[3] with specific uses in mirror backing paints to protect the Cu or Ag films,^[6,7] and also in wood treatment products.^[8] In air, zinc carbodiimide will decompose to zinc oxide between 150-530 °C, but under inert gas it is stable up to 800 °C.^[2, 5] However, when heated to 1100 °C under inert gas it will decompose with loss of zinc vapor to form ‘bamboo like’ nitrogen doped carbon nanotubes of 50 nm in diameter and several microns in length.^[5, 9]

Despite its synthesis and use since the early 20th century, the structure of zinc carbodiimide was not reported until 2001 by Becker and Jansen.^[10] These authors found that it crystallizes in a tetragonal $I\bar{4}2d$ unit cell with lattice parameters $a = 8.805 \text{ \AA}$ and $c = 5.433 \text{ \AA}$, and is composed of a network of corner sharing ZnN₄ tetrahedra, which is ‘reinforced’ by the N-C-N carbodiimide linkages, as seen in Figure 1. This results in each nitrogen atom being in an approximately trigonal planar environment, coordinating to two zinc atoms and a carbon

atom. The carbodiimide unit is symmetric (with both C-N bonds of equal length) but slightly bent, with a bond angle of 176.3° . Becker and Jansen described the nearest analogous structure as being the high pressure structure of Willemite,^[11] but with exchange of nitrogen for oxygen, removal of silicon and insertion of carbon to generate the carbodiimide ion.

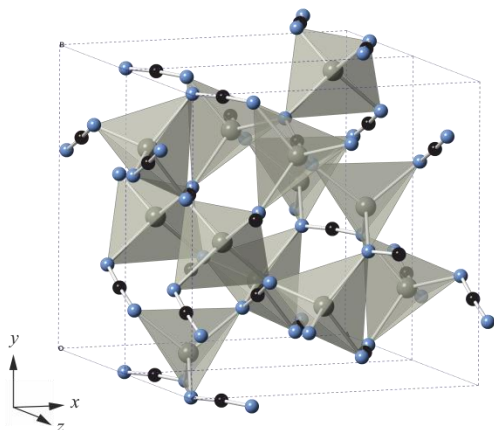


Figure 1. Representation of the crystal structure of ZnNCN, as determined in reference 10, showing the corner sharing network of ZnN_4 , with NCN carbodiimide linkages. Zinc ions are shown in gray at the center of the tetrahedra, nitrogen in blue at the corners of tetrahedra, and carbon in black linking the nitrogen atoms.

The carbodiimide ion itself can be considered as a pseudochalcogenide, with charge and size requirements similar to that of the sulfide ion, but with harder nitride bonding interactions. Although for historical reasons ZnNCN is often referred to as zinc cyanamide in the literature, modern convention is that the symmetric unit, with the formal Lewis structure $N=C=N^-$, present in ZnNCN, is properly termed the carbodiimide ion. The cyanamide ion is the lower symmetry $N\equiv C-N^{2-}$ structure, with inequivalent carbon-nitrogen bond lengths, found, for example, in lead cyanamide.^[12] The majority of solid state materials containing the $(NCN)^{2-}$ ion, however, are carbodiimides. These have been extensively studied in recent years by the group of Dronskowski with an interest in using the NCN linker to communicate electronic and magnetic information between the metal centers.^[13,14] Their focus has been on

transition metal carbodiimides in the +2 oxidation state, $MNCN$ where $M = Mn, Fe, Co, Ni, Cu$.^[13,15-17] These all adopt a layered structure with sheets of MN_6 edge sharing octahedra linked by carbodiimide units, which is also found in the carbodiimides of Sr, Ba, Hg and Cd.^[18-20] Cobalt carbodiimide has also recently been investigated as a potential electro- and photo- water oxidation catalyst, and is found to have a higher activity than the widely used Co_3O_4 water oxidation catalyst.^[21]

The method of thin film synthesis used in this work, aerosol assisted CVD, is an atmospheric pressure chemical vapor deposition variant in which the precursors are delivered to the reaction chamber *via* an aerosol mist rather than using vapor delivery, and is being increasingly used for thin film formation.^[22-25] It provides advantages over conventional chemical vapor deposition in that film precursors must only be soluble in the chosen solvent, rather than volatile, and precursor ratio in multisource systems can be directly controlled. For the purposes of this work it allows access to urea as a precursor, which would otherwise be unsuitable for more conventional chemical vapor deposition as it has poor volatility and is unstable in the gas phase, decomposing into ammonia and isocyanic acid.^[26]

Despite the resurgence of interest in solid state carbodiimides and their functional properties, we believe that this is the first reported synthesis of such a material as a chemical vapor deposition grown thin film. We will show that the concerted reaction of zinc acetate and urea leads to formation of zinc carbodiimide between 375 and 500 °C, with films characterized using X-ray diffraction (XRD), IR spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

Results and Discussion

Initial characterization of the ZnNCN film. Our preliminary investigations identified that the aerosol assisted CVD of zinc acetate and urea (molar ratio 1:3) can be used to form thin films of zinc carbodiimide at 450 °C. In the absence of urea, zinc acetate in methanol is a route to thin films of zinc oxide.^[27] However, the introduction of 3 molar equivalents of urea leads to the exclusive formation of an adherent and translucent white film of zinc carbodiimide. The film passed the Scotch tape test, although it could be removed with a steel stylus. Side-on SEM determined the thickness of film as 960 nm, measured at 6 cm from the leading edge of the substrate.

Low resolution powder X-ray diffraction patterns for the white film obtained were collected using a Bruker GADDS diffractometer at 10 points along the substrate at 1 cm intervals. These revealed diffraction peaks which could be indexed to the previously published structure of zinc carbodiimide,^[10] with no indication of peaks originating from zinc oxide. A single point 6 cm from the leading edge of the substrate was selected for collection of a high resolution diffraction pattern using a Rigaku SmartLab diffractometer. This dataset was analyzed using Rietveld refinement, with the previously published structure as a starting model. A good fit to the data was achieved after refining the background, profile, lattice, atomic and thermal parameters, and preferred orientation, with goodness of fit parameters of $\chi^2 = 5.2$ and wR_p of 4.0%. This is shown in Figure 2(a). There was no indication of any peaks corresponding to the most likely contaminant, zinc oxide, or any other secondary phase. The broad background feature observed between 15° and 40° 2 θ was due to scattering from the amorphous glass substrate. The refinement of the atomic parameters did not lead to a significant shift in atom positions compared to the published structure, and the isotropic U

thermal parameters were reasonable [Zn 0.0303(5) Å², C 0.016(6) Å², N 0.036(4) Å²]. The sample showed some evidence of preferred orientation, but when this was refined with the spherical harmonic model a texture index value of only $J = 1.23$ was found, a particularly moderate value in the context of thin films.^[28,29]

The refined lattice parameters were $a = 8.777(1)$ Å, $c = 5.407(1)$ Å giving a cell volume of 416 Å³, slightly smaller than the 421 Å³ found in the previously published structure. However, this is less than a 0.5% reduction in the a and c lattice parameters, possibly due to a small variation in composition, or stress within the thin film. To test this we conducted a Williamson-Hall analysis of the line widths. This takes advantage of the different angular dependence of the size and strain contributions to peak broadening, such that in a plot of $\sin\theta$ against $B\cos\theta$, where B is the full-width half-maximum of the peaks, the intercept is inversely proportional to the size of the coherent diffracting domains, and the gradient is proportional to the lattice strain. For this we selected the 12 most intense peaks without significant overlap with their neighbors, and using the *fityk* curve fitting software,^[30] modelled the peaks using a pseudo-Voigt function to determine their line breadth. The Williamson-Hall plot shown in Figure 2(b) was then used to determine the average crystallite size of 28(3) nm and lattice strain of 0.26(4)%. This indicates that there is lattice strain resulting in the observed reduction in lattice parameters of the zinc carbodiimide film compared to the values reported for the single crystal.

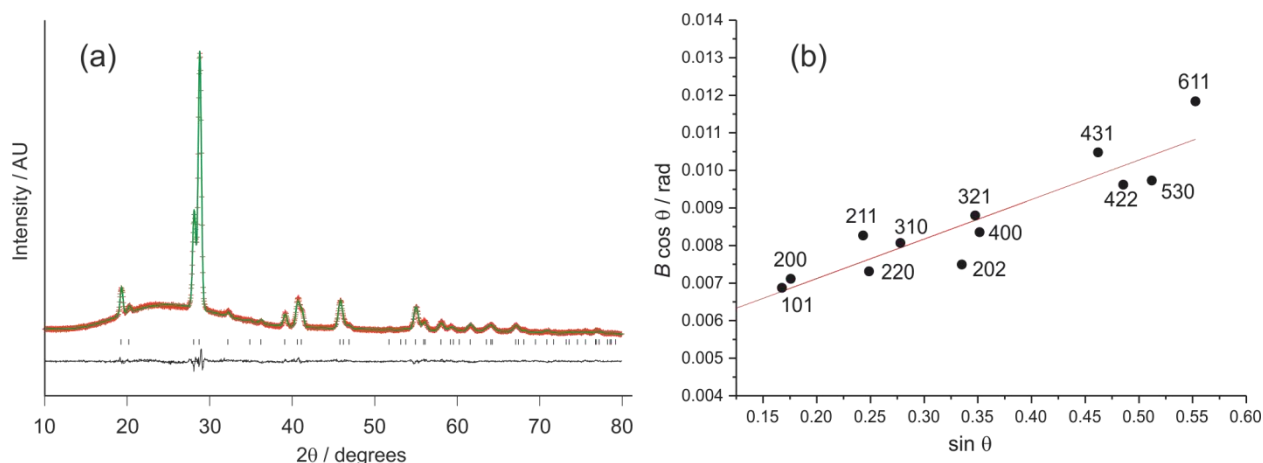


Figure 2. (a) XRD pattern of ZnNCN film on glass, with Rietveld refined fit to the data. Red data points overlaid with model pattern in green, and below the difference curve and tick marks for indexed peaks of $I\bar{4}2d$, $a = 8.777(1)$ Å, $c = 5.407(1)$ Å. (b) A Williamson-Hall plot for this diffraction pattern showing the line of regression used to determine crystallite size and strain.

We can conclude from the diffraction data that a film of zinc carbodiimide has been formed and that this extends across the surface of the substrate. The diffraction data is supported by the FTIR spectrum of the zinc carbodiimide thin film, shown in Figure 3, with absorbance corresponding to the pseudo-independent carbodiimide unit with $D_{\infty h}$ symmetry at 675-695 cm^{-1} , for the Π_u^+ bend, and 1880 to 2170 cm^{-1} for the Σ_u asymmetric stretch. These are consistent with previous reports of zinc carbodiimide,^[3] and also with the IR spectra of the carbodiimides of cobalt, nickel and manganese.^[13,17] If the asymmetric $C_{\infty v}$ cyanamide unit was present an additional absorbance at ~ 1200 cm^{-1} would be observed.

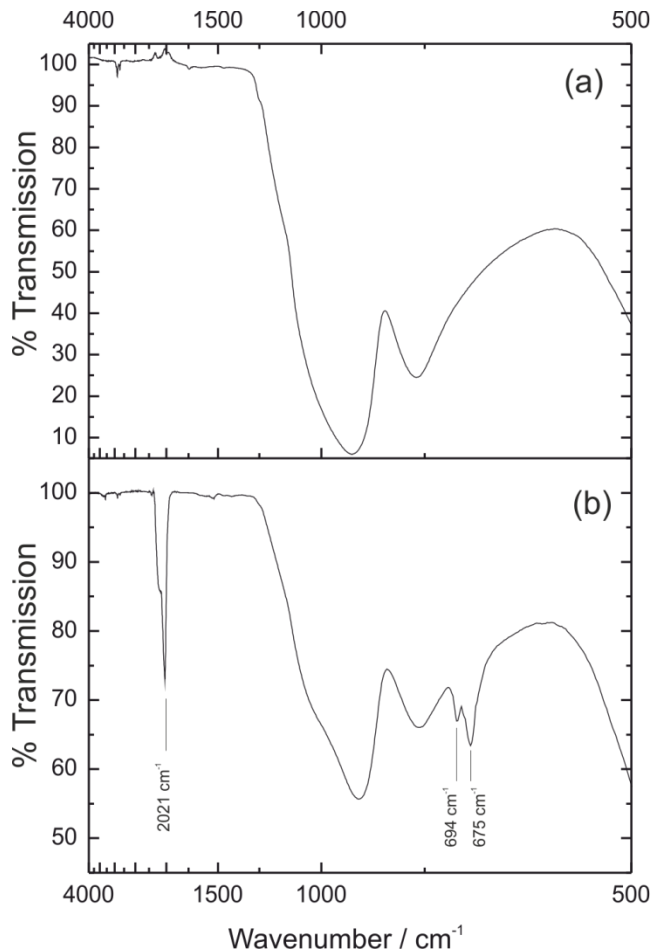
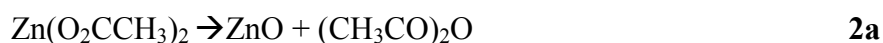


Figure 3. FTIR spectra of (a) glass substrate (the small peaks found over 2000 cm⁻¹ are due slight surface grease contamination) and (b) zinc carbodiimide film on glass. Absorption peaks at 1880-2170 cm⁻¹ and 675-695 cm⁻¹ correspond to the pseudo independent vibrations of the carbodiimide unit. Reciprocal scale used on wavenumber axis to highlight the crucial peaks in the 500-1000 cm⁻¹ region.

The film was also analyzed using EDX, at an electron beam acceleration voltage of 5 kV. This identified that the film was composed exclusively of zinc (27.8±0.1 atom%), carbon (29.7±0.4%) and nitrogen (36.9±0.7%), with small amounts silicon (1.2±0.1%), aluminum (0.7±0.1%) and oxygen (3.8±0.1%) with the last three most likely due to breakthrough of the electron beam into the glass substrate, or surface contamination with dust. This gives a composition for the film itself of ZnC_{1.06}N_{1.33}, significantly underestimating the nitrogen

content compared to the X-ray diffraction model. This is due to surface roughness and collection without internal standards leading to inaccurate quantification of the light elements. However, the EDX does confirm the presence of zinc, carbon and nitrogen, supporting the interpretation of the diffraction data.

The XRD, IR spectroscopy and EDX data all confirm the presence of a phase pure zinc carbodiimide film made from zinc acetate with a threefold excess of urea at 450 °C. Two possible reaction schemes for this are considered below; direct formation through reaction of the zinc acetate and urea, or a two stage process in which the zinc acetate decomposes to zinc oxide, followed by reaction with the urea to form the final carbodiimide film. In both cases we assume the methanol to be an inert carrier. The two stage reaction is plausible, as the formation of zinc oxide is of course known, and a previous report has identified the conversion of bulk zinc oxide to zinc carbodiimide using urea, although this required prolonged exposure at 135 °C, just at the melting point of urea.^[4] To test this an additional experiment was conducted in which a zinc oxide film was deposited from zinc acetate and methanol, characterized by X-ray diffraction to confirm the presence of a zinc oxide film, then returned to the reactor for exposure to the urea aerosol. Both steps were conducted at 450 °C, and in the urea exposure step the same concentration of urea in methanol was used as in the initial reaction. However, this exposure to a urea aerosol had no effect, indicating that for carbodiimide film formation, under these conditions, the reaction is concerted, requiring the simultaneous presence of both the urea and zinc acetate, thus suggesting **1** as the more likely reaction scheme.



A final experiment considered film formation from the perhaps more obvious direct reaction of cyanamide, H₂NCN, with zinc acetate; however, when these were combined in methanol a white precipitate formed immediately. An attempt was made at film formation, however after complete transfer of the aerosol solution no film had been formed, and analysis of the white precipitate by powder X-ray diffraction revealed it to be bulk zinc carbodiimide. This confirmed that zinc acetate and cyanamide will form zinc carbodiimide, but that this reaction is too labile for use in film formation *via* aerosol assisted CVD.

Reaction	Urea Mass / (mol. eq.)	Reactor Temp / °C	Composition and Coverage of 15 cm Substrate	Cell Volume of ZnNCN
Set 1a	0 g (0)	450	ZnO (15 cm)	-
Set 1b	0.041 g (0.5)	450	ZnO (15 cm)	-
Set 1c	0.082 g (1.0)	450	ZnNCN (6cm) / ZnO (9cm)	419.7(7) Å ³
Set 1d	0.165 g (2.0)	450	ZnNCN (10 cm) / ZnO (5cm)	415.7(2) Å ³
Set 1e*	0.245 g (3.0)	450	ZnNCN (15 cm)	416.5(2) Å ³
Set 1f	0.409 g (5.0)	450	ZnNCN (Front 7 cm)	416.9(5) Å ³
Set 2a	0.245 g (3)	375	ZnNCN (Rear 10 cm)	416.9(2) Å ³
Set 2b	0.245 g (3)	400	ZnNCN (15 cm)	414.5(1) Å ³
Set 2c	0.245 g (3)	425	ZnNCN (15 cm)	417.3(1) Å ³
Set 2d*	0.245 g (3)	450	ZnNCN (15 cm)	416.5(2) Å ³
Set 2e	0.245 g (3)	475	ZnNCN (Front 10 cm)	416.1(1) Å ³
Set 2f	0.245 g (3)	500	ZnNCN (Front 10 cm)	415.5(2) Å ³

Table 1. Summary of the reaction conditions, for experimental Set 1 and Set 2. (*) Note that 2d is the same sample as 1e. Composition and substrate coverage determined using multipoint X-ray diffraction, while cell volume data is listed for zinc carbodiimide samples from Rietveld refinement of high resolution diffraction data. All samples made using 0.25 g of zinc acetate dissolved in 40 ml of MeOH.

Effect of urea concentration and temperature on film composition. After determining that zinc carbodiimide could be synthesized, additional experiments considered the effect of

varying the concentration of the urea, and the temperature of deposition. The first series of experiments (Table 1, Set 1) maintained the deposition temperature at 450 °C, and the precursor solution of 0.25 g of zinc acetate dissolved in 40 ml of methanol, but initially without the addition of urea, and then varying amounts up to 5 mol equivalents (mol eq.) relative to the zinc acetate. As the amount of urea was increased, the visual appearance of the films changed, with the compositional variation being measured using low resolution multipoint X-ray diffraction data (summarized in Table 1). In the absence of urea a film was formed across the whole of the substrate, but with a black/brown contamination. The multipoint X-ray diffraction data indicates the presence of zinc oxide at all points across the film, with the color likely due to the incorporation of amorphous carbon arising from the decomposition of either methanol or precursor ligands at the high substrate temperature, in the absence of oxygen. When 0.5 mol eq. of urea was added to the precursor solution this color disappeared and a transparent film was observed across the whole substrate, with only interference fringe colors observable. The X-ray diffraction data still indicates the presence of only zinc oxide, with no peaks associated with zinc carbodiimide. This implies that at this concentration the urea is insufficient to form the carbodiimide, but does remove or prevent the carbon contamination by acting as an *in-situ* oxidant. At 1 mol eq. of urea a ‘tide-mark’ was observed 6 cm from the reactor inlet, in front of which the deposited film was no longer transparent but instead translucent white in appearance without interference colors, whilst beyond it the film remained transparent with interference fringe colors. The X-ray diffraction patterns indicate that this optically dense front region is zinc carbodiimide, while the rear section is transparent zinc oxide. At 2 mol eq. a similar pattern was observed but with the translucent region of zinc carbodiimide extending over the first 10 cm of the substrate. At 3 mol eq. of urea, zinc carbodiimide covers the entire 15 cm substrate. At the highest urea

concentration of 5 mol eq. the zinc carbodiimide was found only over the first 7 cm of substrate, with no coating of any material on the remaining 8 cm.

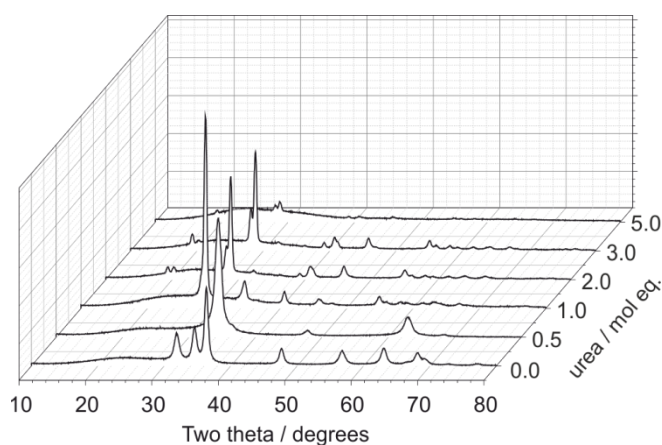


Figure 4. Diffraction patterns recorded using Cu K_{α} radiation on spots of the substrate 6 cm from the reactor inlet, for films synthesized from zinc acetate in methanol solution at 450 °C with varying concentration of urea (Table1, Set 1).

In the second series of experiments, Table 1 Set 2, the urea concentration was held constant at 3 mol eq., but the temperature of the substrate was varied from 375 °C to 500 °C. The low resolution X-ray diffraction scans showed no indication of zinc oxide at any temperature, with the only difference between the temperatures being the extent to which the substrate was coated. This could be observed visually but was also supported by the X-ray diffraction patterns. The lowest deposition temperature, 375 °C, had no coating on the first 3 cm, but with a zinc carbodiimide film covering the rest of the substrate. At 400 °C, 425 °C and 450 °C a film of zinc carbodiimide was found evenly dispersed across the whole substrate. At the higher temperatures the film did not extend across the whole substrate, being found on only the first 9 cm at 475 °C and the first 8 cm at 500 °C.

High resolution X-ray diffraction patterns were recorded for each film from both sets of experiments on a spot 6 cm from the reactor inlet. These were analyzed using Rietveld refinement to determine lattice parameters, and also using Williamson-Hall analysis of line width to determine particle size and lattice strain. The resulting diffraction patterns for the six films synthesized with varying urea concentration (Table 1, Set1) can be seen in Figure 4. For the carbon contaminated film made without urea the diffraction pattern of zinc oxide was found, with broad peaks and almost no preferred orientation. The film synthesized with 0.5 mol eq. again produced a pattern which could be indexed to zinc oxide, but now with a strong 0001 preferred orientation. At 1.0 mol eq. of urea the pattern is dominated by peaks from the zinc carbodiimide structure, which are also much sharper, indicative of larger crystallite size. However, a small peak at $34.6^\circ 2\theta$ was also identified, corresponding to the 0002 peak of zinc oxide, indicating the presence of the oxide. For the remaining three samples made with 2.0, 3.0 and 5.0 mol eq. of urea, the diffraction patterns contain only peaks corresponding to the zinc carbodiimide structure and no peaks that could be indexed to zinc oxide. For the highest urea concentration the peaks were only weakly observed, as the film extends only over the first half of the substrate, and the pattern was collected from the edge of the film. For the second set of experiments, the films made with 3.0 mol eq. of urea at temperatures of 375 to 500 °C (Table 1, Set 2), all the patterns could be indexed to peaks of zinc carbodiimide, with little preferred orientation and no peaks corresponding to zinc oxide.

Rietveld refinement of the patterns collected on the samples of zinc carbodiimide from all the experiments found no significant variation or trend in lattice parameters with either variation in urea concentration or substrate temperature; values for a ranged from 8.765 Å to 8.784 Å and for c from 5.394 Å to 5.401 Å.

As with our initial sample of zinc carbodiimide, Williamson-Hall analysis of peak breadth was conducted using values of FWHM of the most intense, non-overlapping peaks for each sample of zinc carbodiimide film, except for the films formed using 0 and 0.5 mol equivalents where zinc carbodiimide was the not dominant phase and instead the analysis was conducted on peaks corresponding to the dominant zinc oxide. For all the samples analyzed there was no significant variation or trend in the extent of strain, with all samples showing less than 0.30% strain. However, a more interesting effect is observed in the particle size results. The samples with zinc oxide display a small crystallographic particle size of approximately 9 nm, however all the zinc carbodiimide samples show particle sizes of at least twice this, with values from 21 to 28 nm. Surprisingly we do not see the expected trend of increasing particle size with temperature; instead the particle size of zinc carbodiimide is independent of temperature, and significantly larger than the zinc oxide grown without the addition of urea.

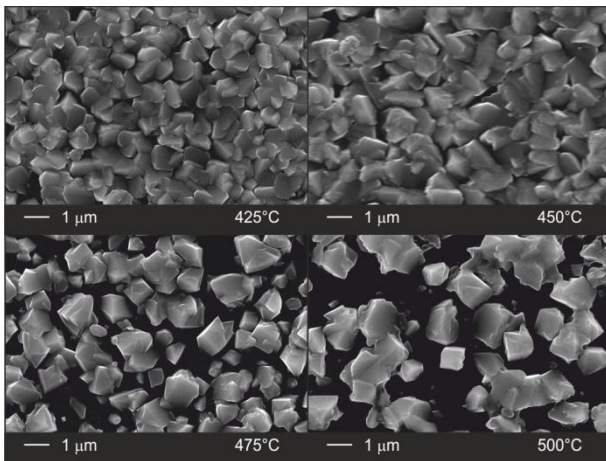


Figure 5. SEM images of the zinc carbodiimide films grown at 425, 450, 475 and 500 °C.

The images are all taken from spot on the film approximately 7 cm from the reactor inlet

The results of the Hall-Williamson analysis are supported by the SEM imaging, results of which are shown in Figure 5. These show evidence of the typical island-growth mechanism

found in CVD, but with the same apparent particle size at synthesis temperatures from 425 to 500 °C. However the density of particles decreases with increasing temperature, although this is an artifact of each image being recorded at the same point on each film – 7 cm from the reactor inlet. At the higher two temperatures only the front 10 cm of the substrate was coated, so these images show the ‘rear’ section of the film, where precursor depletion is leading to a reduced density of crystallites due to lower seeding rates.

Conclusions

We have described a route to the formation of zinc carbodiimide thin films using the aerosol assisted chemical vapor deposition of zinc acetate and urea in methanol solution, and characterized these using X-ray diffraction, IR spectroscopy, scanning electron microscopy and energy dispersive X-ray analysis. We have identified the optimum urea concentration as a threefold excess over the zinc acetate concentration, with an optimum growth temperature between 400 and 450°C, although films can be formed with partial substrate coverage in the range of 375 to 500 °C, with no apparent dependence of particle size on temperature. We have also shown that reaction between zinc acetate and urea must be concerted, and that zinc oxide cannot be converted to zinc carbodiimide under these conditions. This unusual urea decomposition route represents the first time that CVD has been used to synthesize zinc carbodiimide, and holds out the promise of finding routes to thin films of other functional carbodiimide materials in the future.

Experimental Section

ZnNCN film synthesis. The depositions were carried out using a cold walled quartz tube reactor with a semi-circular section carbon block insert acting as substrate holder, heated using a Watlow 750 W heater cartridge, details of which have been published previously.¹⁸ The substrate used was a 40×150×4 mm³ sheet of float glass, with a SiC_xO_y thin film coating to prevent ion diffusion into the deposited film, provided by Pilkington NSG Ltd. An identical piece was suspended 8 mm above it to act as a ‘top plate’ and provide a channel for laminar gas flow through the reactor. Crucially, the reactor exhaust was connected to a Dreschel bottle with 3 cm of silicone oil, to prevent back diffusion of air into the reactor. The precursor solution reservoir was held in a 100 ml three-necked round bottomed flask, suspended above a deionised water bath containing a piezoelectric humidifier (Maplin, product no. L38AK). This generated an aerosol mist of the precursor solution in the round bottomed flask, which was transported to the reactor using argon (BOC, Pureshield) as a carrier gas.

The film precursor solution was zinc acetate (Sigma Aldrich, 99.99%) and urea (Alfa Aesar 99.3+%) dissolved in methanol (Fisher Scientific, Technical Grade). All films were deposited using 0.25 g of zinc acetate dissolved in 40 ml of methanol, with a flow rate of 1 L.min⁻¹ of argon as inert carrier gas. Each reaction was continued until the precursor supply had been consumed, taking approximately 120 mins for each film. The initial set of experiments used a fixed deposition temperature of 450 °C, with amounts of urea varying from 0 to 0.41 g, or from 0 to 5 mol equivalents relative to the quantity of zinc acetate. This identified that the optimum amount of urea was 0.245 g, or 3 mol equivalents of urea, and this was used in the second set of experiments where the deposition temperature was varied from 375-500 °C. A complete list of the deposition conditions can be found in Table 1.

Structural characterization. The films were analyzed by grazing incidence X-ray diffraction, infra-red spectroscopy and energy dispersive X-ray analysis, with scratch tests for adherence. The grazing incidence X-ray diffraction was collected using an incident angle of 2° with two different diffractometers. The first was a Bruker GADDS fitted with a 2D area detector utilizing Cu K_α radiation (45 kV, 40 mA, step size 0.04°) and a programmable *xyz* stage, which allowed for automated scans across multiple points on the film surface, although the optics limited the resolution and also lead to considerable instrumental peak broadening. The second measurement was collected at a single point 6 cm from the leading edge of the substrate, using a Rigaku Smartlab diffractometer, fitted with a rotating anode Cu K_α source (45 kV, 200 mA, step size 0.01°), which allowed for higher resolution data for Williamson-Hall analysis of peak broadening, and Rietveld refinement for structural data.

Energy dispersive X-ray spectra were collected using a Philips XL30 SEM with a 5 kV accelerating voltage, in environmental mode. Infra-red spectra were recorded in the range of $400\text{-}4000\text{ cm}^{-1}$ using a Perkin-Elmer Spectrum 65 FTIR fitted with a Specac Golden Gate ATR.

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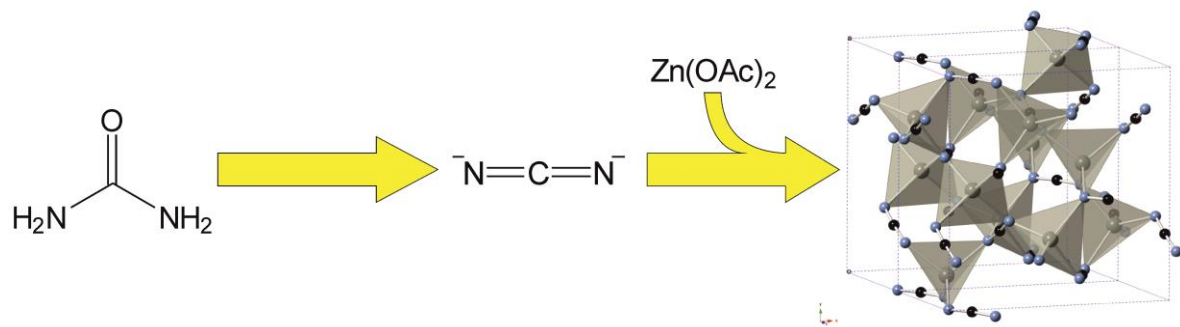
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ToC figure



SYNOPSIS

The concerted aerosol assisted chemical vapor deposition reaction of urea and zinc acetate in methanol allows formation of zinc carbodiimide thin films. This can be achieved over a substrate temperature range of 375 to 500 °C with a minimum excess of 2 mol equivalents of urea needed for pure ZnNCN , and an excess of up to 5 mol equivalents tested.