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Aerosol Assisted Chemical Vapour Deposition of Transparent Zinc Gallate Films

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Aerosol assisted chemical vapour deposition (AACVD) reactions of GaMe₃, ZnEt₂, and 6 equivalents of the donor functionalized alcohol, HOCH₂CH₂OMe, in toluene resulted in the deposition of amorphous transparent zinc gallate (ZnGa₂O₄) films at a range of temperatures (350 - 450 °C). The zinc-gallium-oxide films were analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDX), glancing-angle X-ray powder diffraction (XRD) and optical studies.

Introduction

In recent years there has been a surge in the development of catalysts to be used in the field of photoelectrical water splitting, since these methods often offer clean and efficient alternatives to generating electricity.^[1-4] The world's energy demands are ever increasing; it is not just essential to find renewable energy alternatives but also to improve processes that will stabilize atmospheric CO₂ levels. The current rates of water splitting are low, and whilst the conversion of sunlight into fuel *via* water splitting is a known technology, there is much research into improving this area.^[1]

ZnGa₂O₄ has seen much discussion in the last decade owing to its potential application in water splitting,^[1] degradation of pollutants,^[2] photoreduction of CO₂,^[3] and as reflective optical coatings in the aerospace industry.^[4] It is well reported both in experimental and theoretical investigations that photocatalysis of zinc gallate has been used extensively in photoelectrochemical water splitting,^[5] dye sensitized solar cells,^[6] and various other applications.^[7,8]

The adsorption and subsequent decomposition of water on ZnGa₂O₄ has been investigated previously, and a DFT study showed that water adsorption and decomposition were surface structure dependent.^[9] Further afield these materials, when doped, have application as phosphors.^[32] ZnGa₂O₄ crystallizes in the space group *Fd3m*, with a close packed face centered cubic structure.^[10] The Ga³⁺ ion occupies the octahedrally coordinated sites, whilst Zn²⁺ occupies the tetrahedral sites.^[11]

The optimum growth temperature was found to be 450 °C, which produced transparent films with excellent coverage of the substrate. XPS confirmed the presence of zinc, gallium and oxygen in the films. Annealing these films at 1000 °C resulted in crystalline films and glancing-angle powder XRD showed that a zinc gallate spinel framework with a lattice parameter, *a* = 8.336(5) Å, was adopted.

Luminescence of ZnGa₂O₄:Cr³⁺ has shown a vast improvement when substituting the traditional chromium or manganese dopant to a germanium or tin dopant. The synthetic methods employed to isolate these spinel solid solutions often include multi step synthesis, requiring high temperatures over several days. Moreover the optical properties of zinc gallate depend on the synthetic conditions. A wide range of methods have been employed, including thermal vaporization, sol gel and high-frequency RF ion plasma sputtering methods (for thin films) and hydrothermal and glycothermal (for solids).^[12,13]

Whilst traditional spinel synthesis is a laborious process, with the synthesis of ZnGa₂O₄ spinel including lengthy experimental procedures and high temperatures (1200 °C)^[15] chemical vapour deposition (CVD) is a viable alternative that has been used recently for the synthesis for CuGa₂O₄.^[17] CVD is usually limited simply by precursor requirements, for example volatility in atmospheric pressure (AP)CVD, or solubility in aerosol assisted (AA)CVD. The range of potentially applicable precursors is vast, and the solution based precursors, formed *in situ*, used in this report are well reported.^[16]

In addition, AACVD allows for control of film morphology and composition suggesting that selective growth of surfaces is possible. We have previously investigated CVD methods for the deposition of transparent conducting oxides (TCOs), photocatalysts and gas sensors:^[18] including Ga₂O₃,^[19-25] In₂O₃,^[26,27] Ga_xIn_{2-x}O₃,^[28,29] In₂O₃:Ti, In₂O₃:Ta^[30] and TiO₂:SnO₂.^[31]

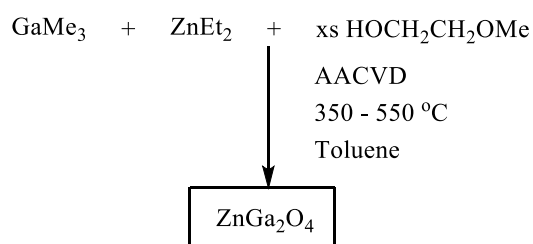
In this contribution we describe the use of readily available chemicals for the deposition of zinc gallate *via* AACVD. Herein we report a novel synthetic route to ZnGa₂O₄ thin films on glass.

Results and Discussion

The AACVD reaction of GaMe₃, ZnEt₂ and the donor functionalised alcohol HOCH₂CH₂OMe on glass and quartz

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substrates was studied between 350–550 °C, according to Scheme 1. For each system, deposition was observed on both the substrate and top plate. The top plate was measured to be ca. 50–70 °C lower in temperature than the substrate. Films deposited on the substrate were used in all analysis. At all deposition temperatures the films showed good substrate coverage, were transparent and strongly adherent (passed the Scotch™ tape test but could be scratched off with a steel scalpel). The resulting films in all instances were found to be thin (ca. 300 nm), of uniform thickness and at 450 °C were deposited across the full length of the substrate. The deposited films were insoluble in common organic solvents, but quickly decomposed in nitric acid. Additionally four-point probe measurements suggest that the films were not electrically conductive at room temperature. Unlike most films prepared via AACVD pre-annealed films did not exhibit a brown tint, indicative of carbon contamination in the films, suggesting that this approach to these thin films limits carbon incorporation.



Scheme 1. Aerosol-assisted chemical vapour deposition of GaMe₃, ZnEt₂ and HOCH₂CH₂OMe in toluene.

The reaction of GaMe₃, ZnEt₂ and excess ROH (R = CH₂CH₂OMe) in toluene was assumed to generate *in situ* organoalkoxometallanes, such as [Me₂Ga(μ-OR)₂ZnEt], or mixtures of [Me₂Ga(μ-OR)₂] and [MeZn(OR)] which would have similar structures to compounds synthesized in solution based reactions described previously.^[36-39] The deposition conditions and analysis of the films grown are given in Table 1.

Table 1. Deposition conditions and analysis of the films grown from the AACVD of GaMe ₃ , ZnEt ₂ and HOCH ₂ CH ₂ OMe in toluene.			
GaMe ₃ :ZnEt ₂ in bubbler	Temperature of deposition (°C)	Surface	EDXA
1:1	350	Film	Zn _{1.4} Ga
1:1	450	Film	ZnGa _{2.6}
1:1	450	Feature	ZnGa _{2.6}
1:1	550	Film	ZnGa _{2.9}
1:1	550	Feature	ZnGa ₃

The gallium-zinc-oxide films were characterized using a range of techniques. Glancing-angle X-ray diffraction (XRD) showed films deposited by AACVD were amorphous at all

deposition temperatures as expected since crystalline films of ZnGa₂O₄ are typically deposited at temperatures >625 °C.^[33-38] With particular relevance to this study, we have previously described the AACVD of GaMe₃, InMe₃ and HOCH₂CH₂OMe, which resulted in the formation of amorphous thin films of gallium-indium-oxide, which on annealing at 1000 °C resulted in highly transparent Ga_{0.4}In_{1.6}O₃ films.^[28,29] Films deposited at 450 °C showed the best coverage of the substrate, with a complete conformal coating and so were also deposited on quartz substrates. These films were subsequently annealed at 1000 °C, which resulted in highly transparent films and glancing-angle XRD showed that the spinel, ZnGa₂O₄ had formed (Figure 1). The broad peak between 15° and 30° is a feature of the silica substrate, often observed in glancing angle XRD, particularly with thin films. Interestingly, annealing had no effect on the morphology of the films, although this could be a result of the film thickness. It has previously been reported that crystalline ZnGa₂O₄ films are deposited at temperatures above 625 °C, but that annealing above 650 °C results in the formation of β-Ga₂O₃ along with ZnGa₂O₄.^[39] For the films described herein and annealed at 1000 °C, crystalline β-Ga₂O₃ was not detected by XRD, only single phase ZnGa₂O₄. This could be due to the polycrystalline nature of the material, as evident in the XRD.

The lattice parameter of the material was deduced via a La Bail refinement to be 8.336(5) Å and all peaks were indexed to the cubic spinel ZnGa₂O₄ phase. The lattice parameter matches well with previous literature reports for thin films of ZnGa₂O₄ (8.3342(5) Å).^[34-36,40,41] The most intense peak for the zinc gallate (Figure 1) corresponds to the (3 1 1) plane. No peaks were observed for separate phases of zinc oxide, gallium oxide or gallium-doped zinc oxide in the XRD pattern.

In gallium-doped zinc oxide (ZnO:Ga), only small lattice distortions are expected due to the similar ionic radii of Zn²⁺ and Ga³⁺. However, gallium doping can also result in the formation of spinel structures (M^{II}Ga₂O₄), particularly when the matrix to be doped is ZnO and heavily doped samples are formed. In the normal spinel structure of ZnGa₂O₄, the Zn²⁺ ions occupy tetrahedral sites and Ga³⁺ ions the octahedral ones. A previous report describing the deposition of gallium-doped zinc oxide or spinel ZnGa₂O₄ via the plasma-enhanced CVD of ZnEt₂ and GaMe₃ in an oxygen plasma found that the ratio of the organometallic precursors had a significant effect on the phase obtained.^[44] Films deposited when the gallium fraction was ≥ 50% resulted in insulating films that adopted the ZnGa₂O₄ spinel structure, whereas ≤ 40% gallium precursor yielded conductive gallium-doped zinc oxide. It is therefore likely that the ratio of the organometallic precursors used in the AACVD experiments (~1:1 ZnEt₂:GaMe₃) had a significant impact on the phase of material produced with the relatively high gallium addition affording ZnGa₂O₄ films.

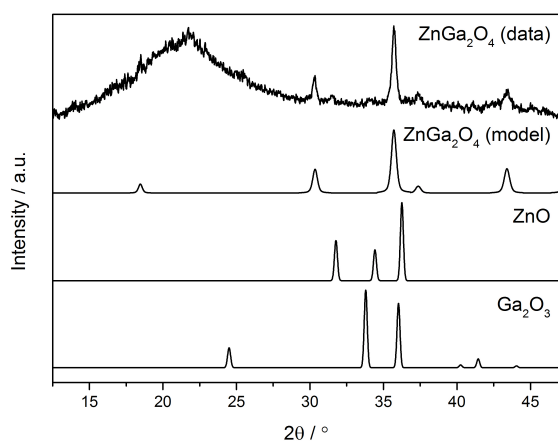


Figure 1. XRD of a film of ZnGa₂O₄, deposited on quartz at 450 °C and annealed at 1000 °C, a generated model of ZnGa₂O₄, and for comparison, standards for ZnO and Ga₂O₃.

Energy dispersive X-ray analysis (EDXA) confirmed the presence of gallium, zinc and oxygen, however breakthrough to the underlying glass substrate was observed in all instances as the films were thin and therefore the metal to oxygen ratios could not be accurately deduced. No carbon was detected in EDXA experiments so carbon contamination levels as a direct result of the precursors and solvents used were suitably low (typically 1at.% detection level).

Films grown at 450 °C and annealed at 1000 °C were found to have a Zn to Ga ratio of 1:2.6 from EDXA. The observed Zn:Ga ratio by EDXA was consistent in all areas of the film and suggests the possible formation of the spinel oxide ZnGa₂O₄ (Zn:Ga 1:2) along with a secondary phase, which is likely to be Ga₂O₃, accounting for the presence of excess gallium. The formation of ZnGa₂O₄ is consistent with the XRD data and the proposed presence of Ga₂O₃ corresponds with previous reports where higher temperatures yielded crystalline ZnGa₂O₄ along with amorphous Ga₂O₃.^[42]

Films grown at 350 °C were the only instance where the zinc content was higher than the gallium, with a Zn to Ga ratio of 1.4:1, however coverage of the substrate was poor, suggesting low temperature results in incomplete deposition. Films grown at 550 °C and annealed at 1000 °C showed the lowest Zn content, with ratios of Zn to Ga, in all areas of the film, being 1:3.0. The increase in the zinc to gallium ratio with increase in substrate deposition temperature can be assigned in part to the volatility of the precursors used. ZnEt₂ is less volatile than GaMe₃, which would, in turn, oxidize more readily, particularly at higher temperatures.

At all deposition temperatures films were smooth, transparent, and had no detectable carbon content. The films are featureless, but after scanning large areas of the films at fairly low magnification (×900) a few surface defects can be found (Fig 2), but these small areas only help to highlight the smoothness of the film. At higher magnification (×6000), the feature of the film is more clearly observed (Figure 2, right) and EDXA results showed this to have similar composition to the rest of the film. It is possible that these features are a direct result of cracks forming in the underlying film being used as nucleation points for further film growth, supporting the

proposition that films were deposited *via* an island growth mechanism.

SEM images of the zinc-gallium-oxide thin films deposited on quartz at 450 °C and annealed at 1000 °C overnight showed that they were identical in morphology to those deposited at 550 °C. The films were featureless, but again after scanning large areas of the films, surface defects could be found, although EDXA analysis indicates that these areas have a similar composition to the rest of the film.

In thicker films analysed, surface defects were found to be larger in area, on closer inspection of these films (Figure 3) crystallite growth is evident as a direct result of annealing. At lower magnification (×6000), islands of film are evident (Figure 3, left), whilst at higher magnification (×40,000) the microstructure is clearly crystalline, showing individual clusters that have grown and agglomerated as islands of the material, indicative of the island growth mechanism of the material (Figure 3, right).

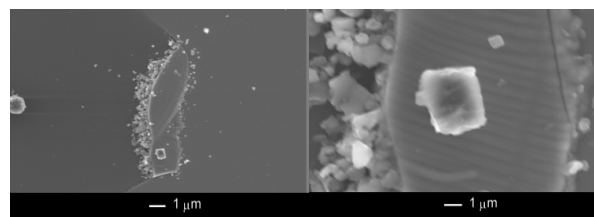


Figure 2. SEM images of zinc-gallium-oxide film deposited at 550 °C.

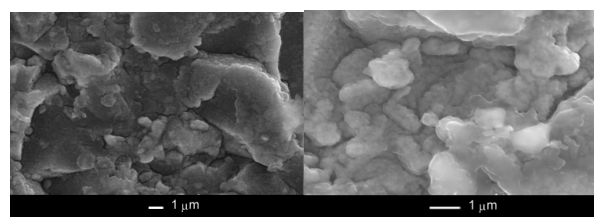


Figure 3. SEM images of features on a ZnGa₂O₄ film deposited on quartz at 450 °C, annealed overnight at 1000 °C.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of the films deposited at 450 °C and annealed at 1000 °C and the whole scanning spectrum indicates the presence of the elements of Ga, Zn and O. The XPS of the films (Figure 4) reveals Ga 2p_{1/2} and 2p_{3/2} peaks at 1144.8 and 1117.9 eV, respectively, in a 1:2 ratio with an energy gap consistent with the value for the element, 26.8 eV^[45,46]. The peaks at 1044.7 and 1021.6 eV correspond to Zn 2p_{1/2} and 2p_{3/2}, respectively, with the peaks in a 1:2 ratio again consistent with literature reports for ZnGa₂O₄.^[43] The presence of these peaks for both gallium and zinc are consistent with those reported previously for ZnGa₂O₄. The O 1s peak in the XPS data can be fitted by a Gaussian distribution, centred at 530.1 eV, which is attributed to the O²⁻ ions in the ZnGa₂O₄ lattice.^[44,45]

The O:Ga and O:Zn ratios, calculated using sensitivity factors determined from the empirical peak area and then corrected for the systems transmission function, were found to give a zinc to gallium ratio for peaks corresponding to ZnGa₂O₄ of 1:2. These results further support the formation of ZnGa₂O₄.

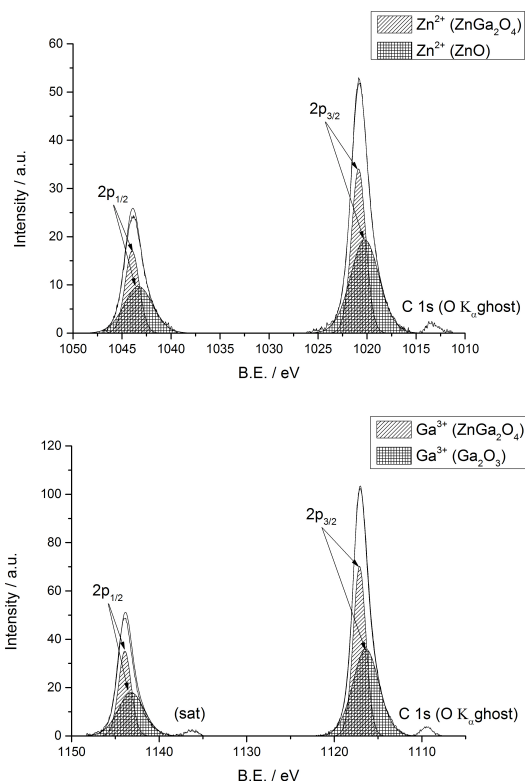


Figure 4. XPS for a film deposited at 450 °C by AACVD from the *in situ* reaction of GaMe₃, ZnEt₂ and excess HOCH₂CH₂OMe in toluene of: *top*, Ga 2p peaks, *bottom*, Zn 2p peaks.

No further impurities were observed *via* XPS which is in contrast to the EDXA results which showed an excess of gallium was present (1:2.6, Zn:Ga). Based on previous reports it is likely that at the temperatures of deposition and annealing, amorphous β -Ga₂O₃ as well as crystalline ZnGa₂O₄ has been formed for these films. EDXA indicated that both Zn and Ga were present in the bulk of the film and the XPS suggests that only zinc gallate exists at the surface. Therefore it is likely that the bulk of the film comprises of ZnGa₂O₄ and amorphous Ga₂O₃, which would account for the excess gallium in the EDXA result, with some surface segregation effects resulting in only zinc gallate (ZnGa₂O₄) being present at the surface (consistent with the surface techniques of XRD and XPS).^[19] A similar effect was observed for ZnGa₂O₄ films deposited by spin coating a sol-gel colloidal suspension, which resulted in a multiphasic material composed of crystallites of ZnGa₂O₄ in an amorphous matrix of zinc and gallium oxides.^[46]

Transmission and reflectance measurements between 200 and 2550 nm showed that the films displayed minimal reflectivity (5–10%) and were highly transparent with transparency ranges from 80% to 90% in the visible. The transmission characteristics of the deposited films were investigated using UV/vis/near IR spectrometry. All films were highly transparent with almost all having average transparencies in the region of 80%.

Conclusions

AACVD of ZnEt₂, GaMe₃ and HOCH₂CH₂OMe resulted in the formation of ZnGa₂O₄, zinc gallate, films on glass. The *in situ* reaction of the reagents eliminates the need for the synthesis, isolation and purification of a single-source metal alkoxide precursor. The EDXA results in combination with powder XRD and XPS suggest the formation of amorphous gallium oxide and zinc gallate in the bulk of the film with surface segregation resulting in only zinc gallate at the surface. Since this is the first report of AACVD of ZnGa₂O₄ to our knowledge, it is possible that facile doping of an array of elements into these spinel systems could be facilitated with ease, using CVD methods, furthermore, as reported in this paper all films do not require further reduction under a flow of H₂ as seen in other reports. The methods described herein offer a viable low cost, low temperature route to functional spinel materials.

Experimental Section

Caution: It should be noted that GaMe₃ and ZnEt₂ are pyrophoric substances, which ignite spontaneously in air and the CVD of these chemicals can potentially be toxic and corrosive. All experimental should be conducted in a fume hood. Following the deposition films are air and moisture stable and are safe to handle as any reactive species leave via the reactor exhaust during the AACVD process.

General procedures - Depositions were carried out under dinitrogen (99.99% from BOC). Precursors were placed in an AACVD glass bubbler and an aerosol mist was created using a piezoelectric device. The solvent mist was transported in a flow of cold nitrogen from the bubbler in an 8-mm gauge pipe to a horizontal bed, cold-wall reactor (internal dimensions 15 cm × 5 cm) fitted with a graphite block containing a Whatman cartridge heater, used to heat the glass substrate. The temperature of the substrate was monitored by a Pt-Rh thermocouple. Depositions were carried out by heating the horizontal bed reactor to the required temperature before diverting the nitrogen line through the aerosol and to the reactor. The glass substrate was SiO₂, precoated (ca 50 nm thick SiO₂ barrier layer) standard float glass (Pilkington, NSG) 15 cm × 4 cm × 0.3 cm. A sheet of polished quartz (4 cm × 1.5 cm × 0.1 cm) was placed on the substrate 2 cm from the front of the reactor to enable a subsequent annealing step at 1000 °C. The substrates were cleaned prior to use, to remove surface grease. Two-way taps were used to divert the nitrogen carrier gas through the bubbler and the aerosol was carried into the reactor in a stream of nitrogen gas through a brass baffle to obtain a laminar flow. The total time for the deposition process was in the region of 30 – 90 minutes. At the end of the deposition the nitrogen flow through the aerosol was diverted and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to less than 100 °C before it was removed. Coated substrates were handled and stored in air. Large pieces of glass (ca. 4 cm × 2 cm) were used for X-ray powder diffraction. The coated glass substrate was cut into ca. 1 cm × 1 cm squares for subsequent

analysis by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX).

AACVD reactions of GaMe₃, ZnEt₂ and HOCH₂CH₂OMe

A large number of AACVD runs were performed in order to perfect the deposition of the ZnGa₂O₄ spinel. Throughout the work the precursor solution was generated *in situ* from the reaction of GaMe₃, ZnEt₂ and excess HOCH₂CH₂OMe in THF or toluene. Trimethylgallium and diethylzinc were supplied by SAFC Hitech and used without further purification. HOCH₂CH₂OMe was procured from Aldrich and was distilled, degassed and stored over molecular sieves. Excess alcohol was used in order to minimize the risk of producing partially oxidized films. The effect of the metal precursor ratio (GaMe₃:ZnEt₂) on film composition was investigated by using different masses of precursor.

Flow rate was initially experimented with and optimised at 1 Lmin⁻¹, in addition a range of temperatures (300 – 550 °C) were attempted for the deposition process. Deposition times for each experiment ranged from 60 to 90 minutes. After deposition, the bubbler was closed and the substrate allowed to cool under a flow of nitrogen. When quartz was used in the deposition process, this was added on top of the substrate before the deposition process, these were annealed for 24 hours at 1000 °C. *Note: when handling GaMe₃ and ZnEt₂ it is advised that they are cooled to -78 °C before adding solvent, this is then allowed to warm to room temperature before deposition.*

Physical Measurements

Powder X-ray diffraction (XRD) patterns were measured on a micro-focus Bruker GADDS diffractometer equipped with monochromated Cu Kα₁ radiation (Kα₁ = 1.5406 Å). The diffractometer used glancing incident radiation (1.5°). The samples were indexed using the GSAS program and refined using the La Bail method and were compared to database standards. EDAX was obtained on a Philips XL30ESEM instrument, and SEM on a JEOL 6301 instrument. High resolution X-ray photoemission spectra (XPS) were recorded on a Kratos Axis Ultra DLD spectrometer at the University of Nottingham, using a mono-chromated Al-Kα (*hν* = 1486.6 eV) X-ray source. A standard wide scan with high resolution large areas (~300 × 700 microns) with pass energy 80 and 20 were used respectively. Binding energies were referenced to an adventitious C 1s peak at 284.9 eV (this peak is due to residual pump oil used in the XPS high vacuum system). The photoelectrons were detected using a hemispherical analyzer with channel plates and delay line detector. UV-vis-NIR spectra were recorded in the range 190-1100 nm using a Helios double beam instrument. Reflectance and transmission spectra were recorded between 300 nm and 2300 nm by a Zeiss miniature spectrometer. Reflectance measurements were standardized relative to a rhodium mirror, and transmission relative to air.

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Keywords: Zinc gallate • zinc gallium oxide spinel • thin films • chemical vapour deposition

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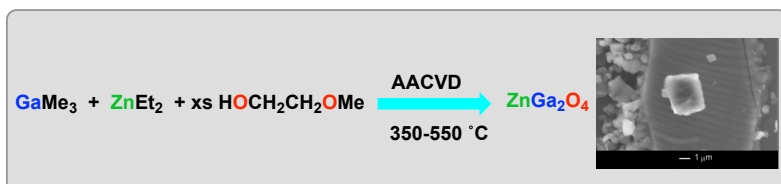
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FULL PAPER



*Dr. C. E. Knapp, J. A. Manzi, Dr. A. Kafizas, Prof. I. P. Parkin and Prof. C. J. Carmalt **

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Aerosol Assisted Chemical Vapour deposition of Transparent Zinc Gallate Films

Transparent zinc gallate films have been deposited via a simple one pot solution based aerosol-assisted chemical vapour deposition (AACVD) method. AACVD of trimethylgallium, diethylzinc and the donor functionalised alcohol, HOCH₂CH₂OMe, in toluene resulted in the formation of ZnGa₂O₄ films along with some amorphous Ga₂O₃. The optimum growth temperature was 450 °C.