R/D 5910-EE-01.

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The Preparation of ACEL Thin Films

by

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R&D 5910-EE-01 Contract DAJA45-88-C-0022

FINAL REPORT

Summer 1988

The research reported in this document has been made possible through the support and sponsorship of the US Government through its European Research Office of the US Army. ~~This report is intended only for the internal management use of the Contractor and the US Government.~~

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Abstract

Zirconium dioxides

Aluminum oxides

Lead Titanates

Details are presented for the chemical vapour deposition of thin films for ACTFEL devices. An aerosol spray pyrolysis process is described for the deposition of insulating oxide layers, ZrO_2, Al_2O_3 and $PbTiO_3$, from acetylacetonate solutions, alkoxides and substituted alkanoates. The general applicability of this process to other oxide layers is clearly demonstrated. The deposition of the active ZnS.Mn layer by atmospheric and low pressure chemical vapour deposition is reported. Zinc diethyl dithiocarbamate, $(Zn((C_2H_3)_2NCS_2)_2$ has been used in both processes. This work has led to the development of the first reported all CVD ACTFEL device structure.

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Introduction

This report covers the continuation of the work initially reported for the periods 15 October-30 November 1987, 1 December 1987-31 January 1988 and 1 February to 31 March 1988.

Thin Film Source Materials

Synthesis

Source materials have been synthesised only when suitable materials are not commercially available. The ASP process has a relatively wide tolerance for source type and this allowed us to employ many commercially available organometallic compounds.

Preparation of Acetylacetonates

The metal acetylacetonates (M = Y, Al, Zr) were prepared using the anhydrous metal halides, dissolved in a suitable solvent, in a quantitative reaction with acetylacetone,

$$\text{e.g.}\quad ZrCl_4 + 4C_5H_8O_2 \longrightarrow Zr(acac)_4 + 4HCl$$

acetylacetone Pet.ether

Preparation of Yttrium 2,2,6,6 - tetramethylheptan-2,5-dione $Y(thd)_3$

$Y(thd)_3$ can be prepared using the anhydrous yttrium halide in reaction with 2,2,6,6-tetramethylheptan-2,5-dione.

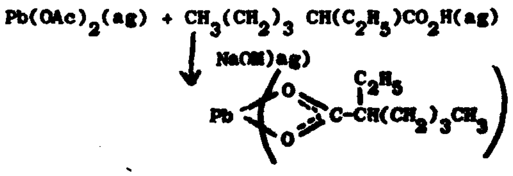
$$YCl_3 + 3thd \xrightarrow{\text{ethanol}} Y(thd)_3 + 3\,HCl$$

Any excess water present prior to the reaction can be removed by the addition of thionyl chloride.

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$$

Preparation of Lead 2-ethylhexanoate

An aqueous solution of sodium hydroxide and 2-ethylhexanoic acid was added to a lead acetate solution, resulting in the formation of a viscous liquid which was characterised as lead 2-ethylhexanoate.

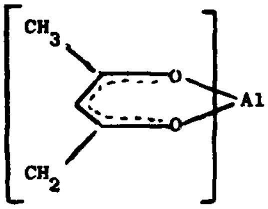


Initial Considerations of Solution Sources for the ASP Process

a) Aluminium Oxide, Al_2O_3

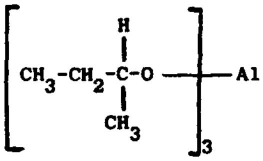
Three principal source materials have been examined in the ASP process:

(i) aluminium acetyl acetonate



$Al(acac)_3$
(pale yellow solid)

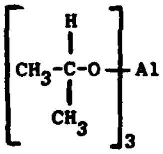
(ii) aluminium s- butoxide



$$\left[CH_3-CH_2-\overset{H}{\underset{CH_3}{C}}-O\right]_3 Al$$

$Al\ (s\text{-}OBu)_3$
(colourless, viscous
liquid)

(iii) aluminium i- propoxide



$$\left[CH_3-\overset{H}{\underset{CH_3}{C}}-O\right]_3 Al$$

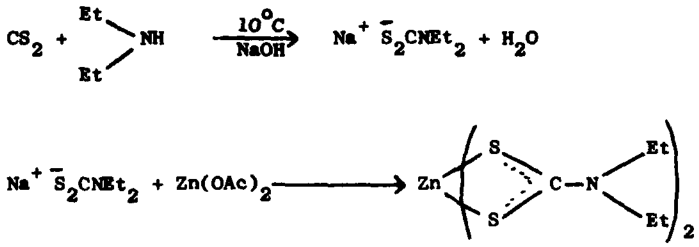
$Al\ (i\text{-}OPr)_3$
(colourless solid)

Initial ASP trials with these source materials indicated that they would all be employed to deposit thin films of Al_2O_3. In a practical consideration, the use of a liquid, e.g. $Al(s\text{-}OBu)_3$, would be most convenient as this would allow us to most easily prepare solutions with few solubility restrictions for the ASP process. However, it was found that the alkoxides such as $Al(i\text{-}OPr)_3$, $Al(s\text{-}OBu)_3$, are extremely moisture sensitive and hydrolysis, with the formation of hydrous oxides readily occurs at the nebuliser, thus preventing its continuous use. $Al(acac)_3$ presented similar problems, but in this case due to its limited solubility in solvents suitable for the ASP process. A suitable

Preparation of Zinc Diethyldithiocarbamate

The zinc diethyldithiocarbamate was prepared by reaction of carbon disulphide and diethylamine under a cold basic regime, and subsequent reaction with an aqueous zinc acetate solution.

(i), (ii)



$$CS_2 + Et_2NH \xrightarrow[NaOH]{10^{\circ}C} Na^+ \bar{S}_2CNEt_2 + H_2O$$

$$Na^+ \bar{S}_2CNEt_2 + Zn(OAc)_2 \longrightarrow Zn(S_2CNEt_2)_2$$

This method can be used to prepare other dialkyldithiocarbamates of zinc. Purification of the product was carried by solvent extraction and recrystallisation, resulting in zinc diethyldithiocarbamate crystals of high purity. The sodium levels were below the detection limits of atomic absorption analysis.

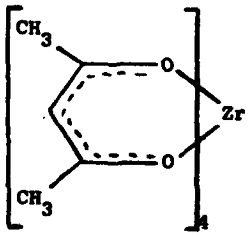
solvent system must be volatile enough to allow complete vapourisation prior to entry into reaction zone, but must not be so volatile as to allow solvent-solute separation at the nebuliser (causing blockages) or too far from the reaction zone thereby resulting in premature decomposition in the gas phase and producing powdery deposits on the substrate.

It was found that solvent mixtures such as 1:3 diacetone alcohol, butanol or butan-2-ol are suitable for the dissolution of $Al(acac)_3$ and will allow continuous operation of the nebuliser. However, this mixture is considerably more difficult to vapourise and even at relatively high substrate temperatures, small scale or localized non-uniform film growth is observed. Further dilution of this mixture with a more volatile solvent, e.g. propanone, and with $Al(acac)_3$ concentrations <0.05M, proved to be suitable for continuous operation of the nebuliser and allowed smooth solvent-solute separation and source decomposition to occur such that clear, defect-free thin films of Al_2O_3 could be produced. Under the present deposition conditions, a 0.03M solution of $Al(acac)_3$ in a 1:3:4 solvent mixture of diacetone alcohol, butan-2-ol and propanone has been determined to be suitable.

b) Zirconium oxide, ZrO_2

ZrO_2 source materials again offered two basic types, the acetylacetonates and the alkoxides. The following have been investigated for use in the ASP system:

(i) zirconium acetylacetonate



$Zr(acac)_4$
(pale yellow solid)

(ii) Zirconium n- butoxide

$[CH_3-CH_2-CH_2 1CH_2-O]_4 Zr$

$Zr(OBu)_4$
(Straw yellow liquid)

Once again, it was found that both source types could be employed in the ASP system but the influence of hydrolysis in the zirconium alkoxides proved to be a limiting factor, and $Zr(acac)_4$ was the preferred choice. A similar solvent system to that employed with $Al(acac)_3$ was found to be suitable, but somewhat higher solution concentrations (up to 0.04M) could be employed without encountering nebuliser blockage problems.

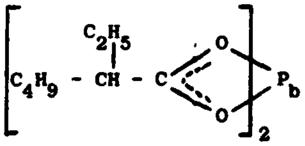
c) Lead Titanate, $PbTiO_3$

Source materials available for investigation were:

Lead acetylacetonates
Lead alkanoates
Titanium alkoxides

As an initial choice for investigation, lead 2-ethylhexanoate and titanium ethoxide were selected for solution and thermal compatibility testing.

(i)



$Pb(2EH)_2$
(viscous colourless liquid)

(ii) $[C_2H_5 - O]_4 Ti$

$Ti (OEt)_4$
(colourless liquid)

This turned out to be a good first choice of source materials, and allowed us to deposit thin films of composition $PbTiO_3$ quite readily and with no particular problems encountered in mist generation. Solutions found to be most effective were 0.025M in each component and made up in a solvent mixture of 20% acetyl acetone, the remainder being propan-2-ol. Carrier gas to the nebuliser was 1:1 $N_2:O_2$ at flow rates of ~3 dm^3/min.

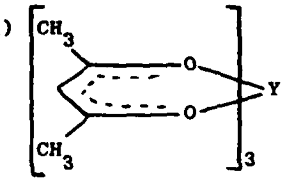
d) Lead Titanate from mixed Alkoxides

$PbTiO_2(OPr)_2$ was synthesised as previously described and dissolved in ethanol to 0.05M. Initial trials with this material did not prove to be very successful, possibly due to it having a relatively high decomposition temperature.

e) Yttrium oxide, Y_2O_3

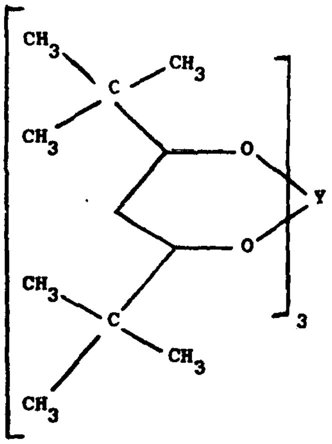
Initial work has centred on the investigation of yttrium acetylacetonate and tris (2,2,6,6-tetramethyl-3,5-heptanedionato) yttrium.

(i)



$Y(acac)_3$
(colourless solid)
m.p. 138-140°C

(ii)



$Y(thd)_3$
(colourless solid)
m.p. 155-159°C

Thus far, only limited success has been obtained in the ASP deposition process, and further work is required to investigate solvent systems and the use of yttrium alkoxides. However, it has been found that both compounds will yield Y_2O_3 thin films if vapourised under low pressure conditions with an air/oxygen bleed gas.

f) Niobium and Tantalum oxides, Nb_2O_2, Ta_2O_5

Source materials of the alkoxides have now been obtained, but these have not yet been evaluated.

$\left[C_2H_5O\right]_5$ Nb, Ta

$(EtO)_5Nb$
(colourless liquid)
m.p. 6°C b.p. 142°C/0.1mm
$(EtO)_5Ta$
(colourless liquid)
m.p. 50°C b.p. 189°C/10mm

In this case, the choice of suitable ASP source materials is relatively limited due to their extreme moisture sensitivity, and modifications to the ASP system are required. Both source materials can, however, be employed in a conventional APCVD system.

Thin Film Deposition

Three deposition systems have been employed:

- (i) ASP (Aerosol Spray Pyrolysis for Insulating Oxides.
- (ii) APCVD (Atmospheric Pressure Chemical Vapour Deposition) for manganese doped zinc sulphide.
- (iii) LPCVD (Low Pressure Chemical Vapour Deposition) for manganese doped zinc sulphide.

(i) ASP:

The ASP process relies on the generation of a fine mist from a solution containing the active component(s), (CVD precursors), the mist being transported by a carrier gas to the heated reaction zone.

The carrier gas, usually a 1:1 oxygen-nitrogen mixture, is employed in the flow range 3-4 dm^3/min. The mist is transported via a stainless steel tube to a horizontal rectangular tube reactor (internal dimensions 37cm length x 4.5 cm width x 2.0cm height) with a 3KW heater placed beneath it.

Glass substrates (dimensions 7.5cm length x 3.6cm width x 1.5mm thickness) with two 3.0mm ITO tracks have been used throughout this work. Sheet resistance of the ITO (measured by linear 4 point probe) is $R_s \simeq 20\Omega/\square$ and thickness $\sim 0.25\mu m$. Substrates are held in the recess of a metal platform specially prepared, with a chromel-alumel thermocouple implanted in the substrate platform, the probe being supported by a stainless tube and fitting approximately 5.0mm below the centre of the substrate.

(ii) **APCVD:**

An APCVD system has been employed to deposit ZnS.Mn thin films from a molten source of zinc diethyldithiocarbamate, with TCM as the vapour source of manganese. The systems were described in previous reports. Both the source and substrate are contained within an ~100cm borosilicate tube of i.d. ~4.8cm, and separated by ~18cm hot zone normally set at the same temperature as the source. This tube is fitted with inlet ports for the main carrier gas flow and TCM vapour, and an exit port for waste gas. Substrates sit in a recess in a high purity graphite platform supported by a stainless steel tube containing a chromel-alumel (CA) thermocouple. The substrate platform is held at a shallow angle ($\sim 5^o$) to the gas flow stream. The source is contained in a rectangular silica boat (~5g max. loading), this being enclosed by a high purity graphite tube with inlet and exit ports such that the carrier gas is directed over the molten source. The graphite source holder is similarly supported by a stainless steel tube with a CA thermocouple, the probe being sited a few mm beneath the silica boat. Two 1KW heaters (~11cm length) are employed to heat the source and substrate. Temperature controllers maintain temperatures of substrate and source holder to within $\pm 1^o$ of the set point. The carrier gas is usually high purity nitrogen, flow rates being controlled by simple rotaflow meters over the range 200-1000cm^3/min in the main flow input line and 10-100cm^3/min in the TCM bubbler. The TCM is contained in an ambient temperature bubbler and is diluted to $5^v/o$ with an inert hydrocarbon solvent such as decalin, to bring TCM vapour concentrations within the correct range with respect to the amount of ZnS being 'cracked out' of the zinc diethyldithiocarbamate. Source temperatures may be employed in the range 180^o(mp = 178^oC) to 230^oC and substrate temperatures in the range 380-450^oC. Typical vapour concentrations are in the range 10^{-5} - 10^{-6} mol/dm^3, for the zinc diethydithiocarbamate. At a substrate temperature of 400^oC, growth rates are ~0.2μm/h. Film uniformity is obviously difficult in a circular section reaction tube, however, over the central region of a substrate, it is within two interference colours over a 3-4cm x 1.5-2.0cm area.

(iii) LPCVD:

In addition to the atmospheric pressure deposition system, thin films of ZnS.Mn have been deposited under reduced pressure conditions. Essentially, this system consists of a 12cm i.d. borosilicate tube, tapering to a 4.8cm i.d. tube at one end. Both ends have broad glass-glass flange end seals. The narrow inlet end has access ports for the input of a bleed gas, TCM vapour, a stainless steel tube with an enclosed thermocouple, and a Pirani gauge head. The stainless steel tube/thermocouple is implanted into a graphite source holder enclosing the source material in a silica boat. In this case, the graphite source holder does not have inlet/exit holes for a carrier gas, rather it has multiple (~0.5mm dia.) holes in the lid. The wider diameter tube is fitted with an exit port for waste gases, leading to a liquid N_2 trap, a port for a steel tube (enclosing a thermocouple) implanted in a large graphite substrate platform. This platform will support three 7.5 x 3.6cm ITO/glass substrates. Heating the substrate platform is via a 12cm dia. x 45cm length, 3KW tube furnace and a small (~11cm length, 1KW tube heater for the source. The system is evacuated by a 2-stage rotary pump, normally to a base pressure of $\sim 10^{-2}$ torr. Nitrogen gas is the preferred bleed gas with typically 20 torr on the main gas input line and 2.5 torr in a 5% TCM solution, contained within a low pressure bottle fitted with needle valves on inlet and exit ports.

Substrate temperatures have been employed in the range 400-450°C and total pressures in the range 15-25 torr. In this case, the source may be employed at temperatures below its m.p. (~178°C), but within the pressure/temperature ranges investigated to-date, source temperatures of 190-200°C are preferred in terms of film growth characteristics. A typical operating sequence is as follows:

1) pump down the loaded system to $\sim 10^{-2}$ torr.
2) with the TCM bottle closed, heat substrate to ~400°C and maintain until original base pressure is achieved.
3) raise system pressure to 20 torr with mainline bleed gas.
4) raise source temperature to desired value, e.g. 200°C.
5) open set point needle valves on TCM bottle and raise system pressure, e.g. to 25 torr.
6) typical running times are 2-4 hours to sequenced close down.

LPCVD

Source	Temperature	Bleed Gas	Total Pressure	TCM Pressure
$Zn(Et_2dtc_2)_2$ TCM 5% in Decalin	190° ambient	N_2	25 torr	5 torr

Substrate temperature	Time	Deposition Area
400°C	4 hrs.	$81cm^2$

ZnS:Mn thin films deposited on glass substrates at 400°C exhibit only one XRD peak with d = 3.118. This corresponds either with the (111) reflection of the sphalerite structure or the (002) reflection of the wurtzite structure.

Similarly grown films deposited on ASP produced ZrO_2 layers show a diffraction pattern with reduced preferred orientation. Data for this is presented below:

2θ	d	(hkl)	I/Io	ASTM d value
26°48'	3.32	100	6	3.309
28°45'	3.103	002	100	3.128
39°24'	2.285	102	11	2.273
51°33'	1.771	103	10	1.764
59°48'	1.569	004	1	1.564
82°09'	1.172	105	4	1.170

This data indicates that zinc sulphide layers deposited on ZrO_2 assume the wurtzite (hexagonal) structure as opposed to the cubic structure normally produced in deposition processes of similar substrate temperature.

Results and Discussion

ASP Insulating Thin Films

Although only a limited number of materials types have been investigated for deposition by the ASP process, it has proven to be an extremely good technique for the deposition of oxide insulating thin films. Most initial work has been carried out on the deposition of Al_2O_3, ZrO_2 and PbT:O_3. Thus far, the respective acetylacetonate derivatives have proven to be the most successful, thin films with good uniformity and thickness control being achievable in a simple deposition system. In all cases, growth rates are similar and in the range ~0.4-1.0µm/h. Best growth conditions at present are determined as:

	Source Meter	Solvents	Concentration
$PbTiO_3$	lead-2-ethylhexanoate titanium ethoxide	Acac, IPA = 1:4	0.05M
ZrO_2	zirconium acetylacetonate	DAA, IBA 1:3	0.05M
Al_2O_3	aluminium acetylacetonate	DAA, IBA propanone 1:3:4	0.025M

	Deposition Temperature	Growth Rates
$PbTiO_3$	340°C	0.5µm/h
ZrO_2	380°C	0.4µm/h
Al_2O_3	440°C	0.4µm/h

Some XRD data for ZrO_2 and $PbTiO_3$ is presented below:

XRD Analysis

(1) ZrO_2 Thin Films

20	d	I/Io	ASTM d value	phase
15°15'	5.14	20	5.1	M
31°36'	2.829	100	2.85	M
35°20'	2.538	80	2.55	MTC
50°54'	1.792	30	1.81	MT
55°48'	1.646	10	1.66	M

(ii) $PbTiO_3$ Thin Films

Lead titanates as-grown at substrate temperatures 280-400°C are amorphous. Thin films of $PbTiO_3$ were annealed in air at 600°C. XRD patterns show the onset of transition from the amorphous to crystalline state. Three broad bands appear and these can be assigned as follows:

1)	20°-22.5°	-	(001) and (100)	weak
2)	30°-32°	-	(101) and (110)	strong
3)	38°-39°	-	(111)	weak

Annealing of a-$PbTiO_3$ thin films produced a slight opacity compared to the as-grown films. EDAX analysis of these films confirmed the stoichiometric composition $PbTiO_3$.

(iii) Al_2O_3 - analysis of Al_2O_3 thin films is in progress.

Deposition of ZnS.Mn Thin Films

In both atmospheric and reduced pressure systems, the source materials were zinc diethyldithiocarbamate ($Zn(Et_2dtc_2)_2$) and tricarbonyl methyl cyclopentadienemanganese (TCM). Growth rates are similar over the deposition range examined in both systems with 0.15-0.2 µm/h being about average for the best growth conditions (smooth, low scatter films). Typical growth conditions are:

APCVD

Source	Temperature	Carrier Gas	Total Flow Rate	TCM Bubbler
$Zn(Et_2dtc_2)_2$	200°C	N_2	500cm^3/min.	50cm^3/min.
TCM 5% in Decalin	ambient			

Substrate Temperature	Time	Deposition Area
400°C	4 hrs.	27cm^2

Conclusions

In the short time available on this contract, we have clearly demonstrated that it is possible to fabricate a complete ACTFEL device stack entirely by CVD methods. The ASP process has proven to be very successful in depositing uniform thin film insulators with extremely simple, low cost but reliable systems. Because of the nature of the process, a wide range of precursors can be employed, offering the possibility of simple binary oxide thin films or more complex multinary oxide systems. Having solved the initial problems of source and solvent materials selection, good quality Al_2O_3 and ZrO_2 thin films can now be deposited in a routine manner. Thin film materials such as $PbTiO_3$ appear to present an additional problem in that it, and possibly all similar materials, can only be deposited under the present conditions in an amorphous form. However, with the availability of a flash annealing technique, it may be a simple matter to produce films of good crystalline quality. Unfortunately, this equipment is not available to us and annealing experiments were difficult to carry out with any great success due to warping of the glass substrates at temperatures in the region of 500°C.

The growth of ZnS:Mn thin films by AP and LPCVD methods has met with a reasonable degree of success. Growth rates are relatively low, but there do not seem to be any adverse effects when growing ZnS:Mn on oxide layers at elevated temperatures, although structural changes are apparent. Normally, in a CVD process of the type carried out in this work, the ZnS.Mn would be expected to be deposited in the cubic form, but data suggests that growth on ZrO_2 yields hexagonal modification. This is extremely interesting and may allow structural modification of ZnS.Mn thin films to determine its influence on device performance and ultimately improve device efficiency. Finlux have suggested that hexagonal ZnS.Mn deposited by the ALE process are more efficient than cubic films deposited by evaporative or sputtering methods. Also, by appropriate treatment of the first oxide layer, it may be possible to modify grain size and determine its influence on device efficiency.

Clearly, there is still much to be done to move CVD processes into the mainstream of ACTFEL device research and development. The CVD processes employed in this work would appear to offer viable low-cost alternatives to the expensive evaporative or sputtering processes currently in use. However, an intensive 2-3 year development programme will be required to fully realise the potential of these processes. The current 3-monthly renewable contracts are, we believe, actually hindering progress, because long-term plans for CVD systems development, full materials and device characterisation cannot be implemented. Having successfully fabricated the first ever working all CVD ACTFEL device, within the period of two 3-month contracts, it would now surely be appropriate to initiate a higher level continuous programme to optimise deposition control parameters and device materials characteristics.