Metal Organic Chemical Vapour Deposition at CNR – ICTIMA in Padua

G. A. Battiston, F. Benetollo, G. Carta, R. Gerbasi, G. Rossetto, G. Torzo, P. Zanella

Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati (ICTIMA)
Area della Ricerca del CNR, Corso Stati Uniti 4, 35127 Padua, Italy

The ability to obtain a huge variety of thin film materials at low temperatures is the reason of the tremendous expansion of Metal Organic Chemical Vapour Deposition (MOCVD) techniques. Attention has been focused on suitably tailored metal organic precursors to synthesise specific materials. The obtained products are detailed. Oxide thin films (such as TiO_2, ZrO_2, and Al_2O_3) have been deposited either by using new or unusual oxygenated precursors or oxygen free precursors. Metallic films such as platinum, copper, and nickel have also been grown. Some examples of epitaxial semiconductor (III-V) films are reported. Finally, the possibility of achieving a Fe-Ni metal alloy is reported.

Metal Organic Chemical Vapour Deposition (MOCVD) has been shown to be a viable process for the preparation of high quality thin films. Its versatility and the low deposition temperature make the process particularly interesting for industrial applications. Since materials in form of thin films are essential for many advanced technologies, interest and research on MOCVD are continually growing and expanding [1].

The basic step of MOCVD is the decomposition of volatile precursors at a suitable temperature in contact with the substrate on which the desired thin film is deposited while gaseous side products are easily eliminated. The reaction is carried out inside special reactors (thermal, plasma, laser, or photo activated). It is evident that precursors play a crucial role with their peculiar properties:

- Volatility: The precursors must be present in appreciable concentration in gas form inside the reactor in order to assure a fair deposition rate.
- Stability and reactivity: The precursors must be stable both thermally and towards moisture and oxygen to allow easy manipulation. However, they must react under the deposition conditions. Precursors in the liquid phase are preferable (to solid phase) in that they offer more precise control of the evaporation rate than solids because the surface area of a powder cannot be controlled well.
- Purity: This is a crucial requirement especially when electronic grade materials are deposited.
- Environmental compatibility and safety: The precursors should be manipulated without risks for operator safety and environmental contamination.
- Cost: even though reported last, this is a limiting factor for industrial applications.

In recent years synthetic chemistry has been increasingly involved with the aim of producing promising new precursors with tailored properties that have been tested in preliminary research work. The full significance of these efforts cannot be appreciated without a multidisciplinary approach involving the synthesis of precursors, the growth of high quality materials on a large scale, and fundamental studies including thermodynamics, kinetics, chemical engineering, and optimisation of process conditions by using modelling. In this context we have developed our research, and here several recent results will be considered on the following specific subjects.

MOCVD of oxide thin films

Metal oxides form a class of very attractive materials due to the wide range of their technological applications. In principle, their synthesis appears easy and straightforward for the most part of metals even under the MOCVD conditions. The route to the oxides is based on the decomposition of oxygenated compounds (single-source precursors) or on the reaction of oxygen-free metal compounds with oxygenating agents (O_2, H_2O, etc.).

The significant results are summarised in Table 1.

	Precursors	Reactant gas	Source temp.	Growth Temp.	Growth rate	Crystal phase	Ref.
TiO_2	$Ti(OiPr)_4$	O_2	50°C	400°C	~2 µm/h	anatase	[2],[3]
TiO_2	$Ti(OiPr)_4$	N_2, O_2	50°C	120°C Plasma	~1 µm/h	amorphous	[4]
ZrO_2	$Zr[N(C_2H_5)_2]_4$	O_2	30- 60°C	500-580°C	~4 µm/h	monoclinic	[5]
ZrO_2	$Zr[OC(CH_3)_3]_4$	O_2	40°C	350°C	~6 µm/h	cubic	[6]
ZrO_2	$(C_5H_5)_2Zr(CH_3)_2$	O_2, H_2O	70-80°C	400-450°C	~7 µm/h	cubic monoclinic	[7]
ZrO_2-Co_2O_3	$(C_5H_5)_2Zr(CH_3)_2$ $Co(C_5H_5)_2$	O_2, H_2O	70-80°C	400-450°C	~2 µm/h		[8]
ZrO_2-MnO_x	$(C_5H_5)_2Zr(CH_3)_2$ $Mn(hfac)_2THF$	O_2, H_2O	70-80°C	400-500°C	~2 µm/h		[6]
ZrO_2-TiO_2	$Zr[OC(CH_3)_3]_4$ $Ti(O^iPr)_4$	O_2	40-50°C	400°C	1-2 µm/h	cubic	[9]
Al_2O_3	$(CH_3)_2Al(O^iPr)$	O_2	25°C	560 °C	~2 µm/h	amorphous	[10]
Al_2O_3	R_2Al acac R= Me, Et, ^{i}Bu	O_2, H_2O	20-80°C	400-520°C	2-4 µm/h	amorphous	[11]

Table 1: Deposition data of oxide thin films

MOCVD of epitaxial materials

New indium precursors as Et_2InNMe_2 [12] and Me_2InPz [13] (PzH = pyrazole) have been successfully used for MOVPE of InP homoepitaxial layers. The new sources do not present the drawbacks of the conventional $InMe_3$ precursor (high pyrophoricity and high reactivity towards nucleophilic agents), and their lower vapour pressure allows a better control of the epilayer thickness in the growth of MQW structures. Besides, the Me_2InPz has been used in the growth of nanostructures of InP on GaAs substrates obtaining islands of InP with a size distribution peak around 100 nm.

The two-dimensional – three-dimensional transition has been studied for InAs and InP layers grown on (001) GaAs substrates by MOVPE with conventional precursors [14]. The combined use of SFM and RBS allowed the determination of the surface morphology of the samples and of their equivalent layer thickness with a precision better than 0.1 monolayers. The critical thickness for the 2D–3D transition has been found to occur after a deposition of (1.2 ± 0.1) ML for InAs/GaAs, and after a deposition of (2.2 ± 0.2) ML for InP/GaAs, independently of the temperature and of the growth rate. For coverages slightly exceeding 1 ML for InAs, and 2 ML for InP, the surfaces of the samples appear partially covered by small bi-dimensional structures whose dimensions appear to be independent of the system under study and consequently of the misfit.

MOCVD of metallic thin films

Platinum films were deposited at 80 Pa varying the reactor temperature in the range 380 – 420 °C and the sublimation temperature of platinum acetylacetonate ($Pt(acac)_2$) in the range 120 – 180 °C. The molar ratio oxygen/precursor at the inlet was in the 20 – 130 range. The growth rate of 0.4 μm/h above 400 °C was independent from deposition temperatures higher than 400 °C indicating a diffusion limited process. The presence of oxygen led to good-quality metallic films of polycrystalline platinum on all the substrates. The X-ray diffraction patterns always exhibit polycrystalline cubic structure, highly textured in the (111) direction [3].

We prepared new Pt precursors $(C_5H_4CH_3)Pt(CH_2CHCH_2)$ (Methylcyclopentadienyl platinum allyl), complexes of Pt containing methylcyclopentadienyl ($C_5H_4CH_3Pt(CH_3)_3$), and allyl ligands ($C_5H_5PtCH_2CHCH_2$) [15]. Pt deposition was carried out with the first precursor under mild conditions (25 – 30 °C source temperature, N_2 carrier gas, 300 °C substrate temperature). Appreciable growth rate (1.5 – 2.0 μm/h), and a smooth and bright surface were obtained. But the most remarkable feature was the purity of the deposited platinum.

Copper films have been deposited at 100 Pa and 370 °C by using the new precursor $HB(Pz)_3Cu(PCy_3)$ where Pz is pyrazole, and PCy_3 is tricycloexphosphine in nitrogen or oxygen environment; the films resulted homogeneous, adherent to substrate, and without carbon contamination [16]. Traditional precursors as copper(II) acetylacetonate hydrate and hexafluoroacetylacetonate have also been used in oxygen environment either at low or atmospheric pressure MOCVD. The films sometimes resulted carbon contaminated, and the presence of CuO was detected.

Nickel thin films were obtained at 450 °C in N_2 or O_2 environment as polycrystalline films with preferred orientation (111) and little contamination of carbon and nickel oxide by using the new precursor nickel bismethylacetoacetatemethyl [17].

Kinetics and modelling

The control of the film quality is strongly coupled to the control of conditions in the deposition chamber as temperature, gas feed composition, chamber pressure, and gas flow rates. A theoretical study of the kinetics and transport phenomena is the basis for reproducing the desired properties in the film.

Studies of the growth rate were carried out in order to derive the various kinetic control regimes and the corresponding kinetic laws. As an example for the formation of titanium oxide films the developed model considered the occurrence of a heterogeneous reaction in the film formation and a parasitic reaction in the gas phase [18]. It was therefore possible to find the best conditions for high uniformity in the reactor and the correlation between growth parameters and surface properties (Fig. 1).

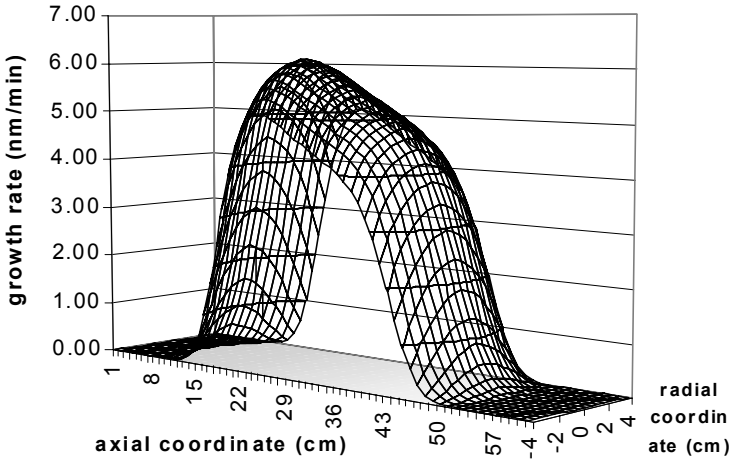

Fig. 1: Growth rate of TiO_2 as a function of position in a reactor pipe with cylindrical symmetry, at 400 °C and 70 Pa.

Optimisation is, in a first instance, a criterion of uniformity regarding some relevant film characteristics, such as thickness, crystallite orientation, adherence, or crystalline phase. Really conclusive results on the optimisation can be achieved only throughout an economic evaluation of the costs on the basis of customer specifications. This kind of evaluation depends on parameters specific of country, man power salary, local law, etc. Also the geometry of reactor plays a fundamental role according to customer requests or process specifications. Modelling is a fundamental step for any economic evaluation. In view of an industrial application, evaluation of costs and economic optimisation of the process have been accomplished [19].

Perspectives of achieving a metal alloy Fe-Ni

As reported in the literature the most promising precursors for Ni deposition are $Ni(CO)_4$, $Ni(dmg)_2$, $Ni(MeCp)_2$, and $Ni(hfa)_2$. Deposition temperature, costs, safety, easy manipulation, growth rate, and a combination of those can steer the choice of a particular precursor.

Precursors for the chemical vapour deposition of iron allow high film purity at temperatures as low as 200 °C. Iron pentacarbonyl $Fe(CO)_5$ was extensively used as precursor with growth rates up to 1 μm/h. Ferrocene $Fe(Cp)_2$ has been studied to a lesser extent because it requires higher deposition temperatures (400 – 500°C) due to its thermal stability.

Only one paper, to our knowledge, deals with co-deposition Fe-Ni via MOCVD. Lane *et. al.* [20] prepared permalloy thin films by using a carbonyl derivative of the two metals as precursors, at atmospheric pressure. The maximum values of magnetoresistance occurred at a composition of about 90% Ni, 10% Fe, and the maximum sensitivity occurred at about 80% Ni, 20% Fe.

The main drawback of Ni-Fe carbonyls is their extreme toxicity that limits their practical use. The design of new volatile precursors of both metals, with comparable chemicophysical properties will be the route to obtain environmentally friendly alloys.

References

[1] a) P. Zanella, G. Rossetto, N. Brianese, F. Ossola, M. Porchia and J.O. Williams, *Chem. Mater.* 1991, **3**, 225.
b) A.C. Jones, P.O' Brien, CVD of Semiconductors, Precursor Synthesis, Development and Applications, VCH, Weinheim, 1996.
c) T.T. Kodas, M. Hampden-Smith, The Chemistry of Metal CVD, VCH Weinheim, 1994. d) M.L. Hitchman, K.F. Jensen, Chemical Vapor Deposition, Academic Press, London 1993.

[2] G.A. Battiston, R. Gerbasi, M. Porchia, A. Marigo, *Thin Solid Films* 1994, **239**, 186.

[3] G.A. Battiston, R. Gerbasi, M. Porchia, A. Gasparotto, *Chem. Vap. Deposition* 1999, **5,** 13.

[4] G.A. Battiston, R.Gerbasi, A. Gregori, M. Porchia, S. Cattarin and G.A. Rizzi, *Thin Solid Films* 2000, in press.

[5] A. Bastianini, G.A. Battiston, R. Gerbasi, M. Porchia and S. Daolio, *Journal de Physique IV, Supplement au Journal de Physique II* 1995, **5**, 525.

[6] G.A. Battiston, R. Gerbasi, and G. Cavinato 5th Italian Meeting on Nanophase Materials, Roma 28-29 October 1999, 63.

[7] S. Codato, G. Carta, G. Rossetto, G.A. Rizzi, P. Zanella, P. Scardi and M. Leoni, *Chem.Vap. Deposition* 1999, **5**, 159.

[8] G. Rossetto et al. in press.

[9] P. Stocco Thesis, University of Padua, 1999.

[10] D. Barreca, G.A. Battiston, R. Gerbasi and E. Tondello, *Mater.Chem*. 2000, *in press*.

[11] G.A. Battiston, G. Carta, R. Gerbasi, M. Porchia, L. Rizzo and G. Rossetto, *J.Phys, IV*, 1999, **9**, 675.

[12] G. Rossetto, R. Franzheld, A. Camporese, M.L. Favero, G. Torzo, D. Ajò and P. Zanella, *J. Crystal Growth* 1995, **146**, 51.1

[13] K. Locke, J. Weidlein, F. Scholz, N. Bouanah, N. Brianese, P. Zanella and Y. Gao, *J. Organometal.Chem*. 1991, **420**, 1.

[14] M. Berti, A.V. Drigo, G. Rossetto and G. Torzo, *J. Vac. Sc. Technol. B* 1997, **15**, 1794.

[15] G. Rossetto, P. Zanella, G. Carta, R. Bertani, D. Favretto and G.M. Ingo, *Appl. Organometal. Chem.* 1993, **13**, 509.

[16] G.A. Battiston, R. Gerbasi, C. Pettinari, A. Drozdov, work in progress.

[17] E. Faggin, Thesis, University of Padua, 1999.

[18] A. Scattolin, Thesis, University of Padua, 2000.

[19] G.A. Battiston, R. Gerbasi, A. Tiziani, A. Figuears and G. Garcia, Mat. Sc. Forum, in press.

[20] P.A. Lane, P.J. Wright, P.E. Oliver, C.L. Creeves, A.A. Pitt, J.M. Keen, M.C.L. Ward, M.E.G. Tisley, N.A. Smith, B.C. Cockaine and H. Harris, *Chem. Vap. Deposition*, 1997, **3**, 97.