



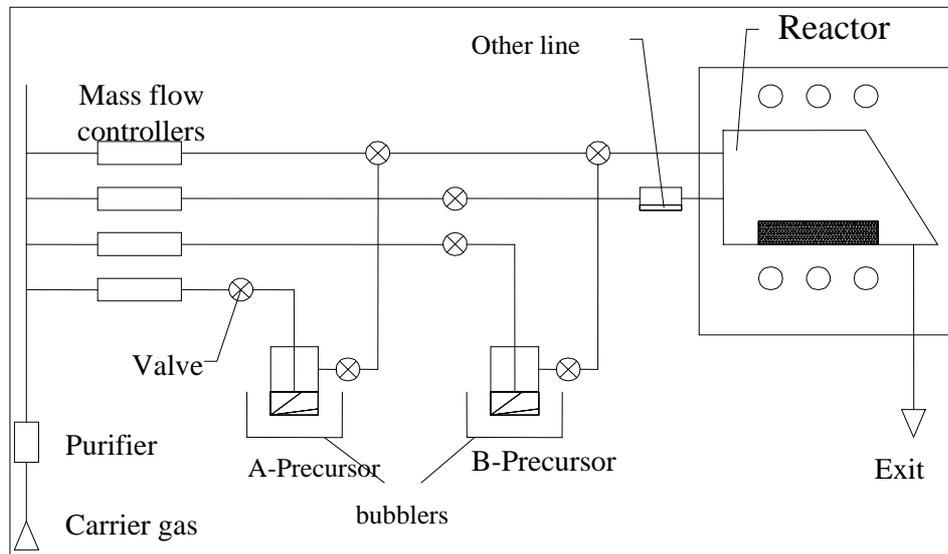
Tecnología de Materiales

Métodos de obtención de capas delgadas

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Basis of MOCVD



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Metal-Organic Chemical Vapour Deposition

Reactor

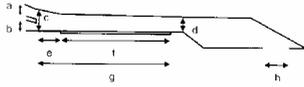
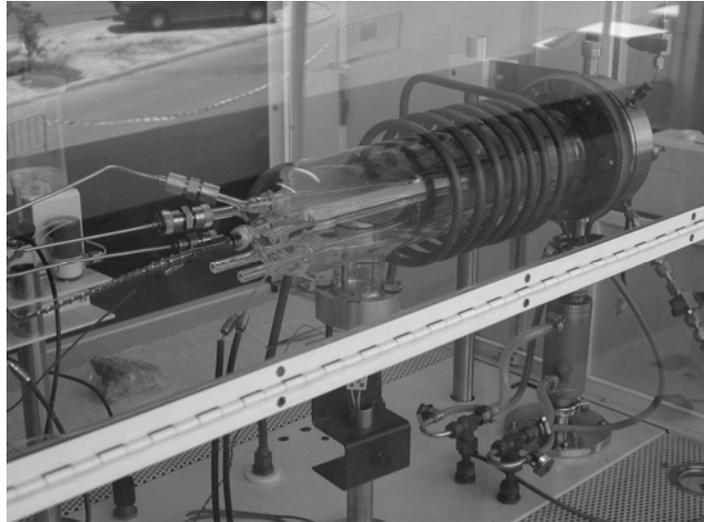


Fig. 1. Scheme of the two-inlet reactor cell: a = upper inlet (15 mm), b = lower inlet (9 mm), c = 19 mm, d = 15 mm, e = 38 mm, f = substrates/wafers (120 mm), g = susceptor (150 mm) and h = outlet (25 mm). Width of the reactor cell is 66 mm.

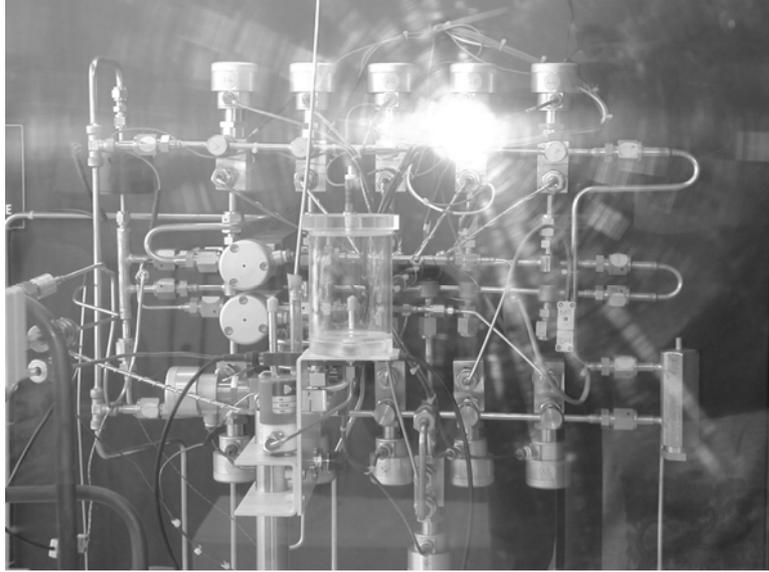


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Metal-Organic Chemical Vapour Deposition

Control
de
gases
al
reactor



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Metal-Organic Chemical Vapour Deposition

General
overview



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Metal-Organic Chemical Vapour Deposition

Control



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Problems as regard the MOCVD process

- Choice of precursors to avoid parasitic reactions
- MOCVD reactor design to facilitate the process
- Substrate and effects on the morphology
- Experimental conditions : Temperature, pressure, carrier gas and so on
- Others...

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Some general considerations

The ethyl radicals have lower reactivity as regard the methyl's ones. Lower C pollution using ethyl radicals
A very important problem is the strong reactivity between Zn and Oxygen. We need to avoid parasitic reactions that can pollute and damage the layer

Lower temperatures are easier to manage for technical reasons
They reduce the effect of tensions in the heating and cooling processes. They also can reduce the concentration of puntual deffects

If we use sapphire as substrate, we have a large mismatch.
In order to avoid the induced problems a good way is the analyse of the different effects related with different substrate orientations and, additionally, the use of buffer layers



¿Que precursores elegir?

BBB versus ASE

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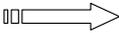


Precursores

Table 3.1 Vapor pressure data for common organometallics (from Epichem Ltd. product data sheets).

Organometallic	<i>A</i>	<i>B</i>	Remarks
TMAI	10.475	2780	9.7 torr @ 20 °C
TEAl	10.784	3625	0.026 torr @ 20 °C
TMGa	8.495	1825	64.5 torr @ 0 °C
TEGa	9.165	2530	3.4 torr @ 20 °C
TMIn	9.735	2830	1.2 torr @ 20 °C
TEIn	8.935	2815	0.44 torr @ 30 °C

Typical values for the molar flow are in the order of 10-20 $\mu\text{mol}/\text{min}$

For TMGa  4.8 sccm at 0 °C

For TEGa  100 sccm at 20 °C

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Diethylzinc

Boiling Point: (244F)118C

Vapor Pressure: $\log_{10} P(\text{mmHg}) = 8.280 - 2109/T(\text{K})$

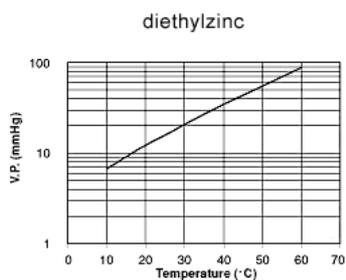
Freezing Point: (-18F)-28C

Liquid Density: 1.206 g/ml @ 20C

Molecular Weight: 123.49 grams

Solubility in water: Reacts violently.

Appearance: Colorless liquid which is pyrophoric.



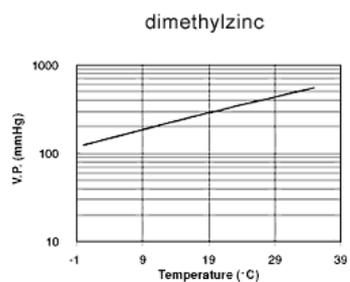
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Dimethylzinc

DIMETHYLZINC PHYSICAL PROPERTIES

Formula Weight:	95.44
Boiling Point:	46°C
Freezing Point:	-42°C
Density @ 10°C:	1.386g/ml
V.P. @ 0°C:	123mmHg
V.P. @ 20°C:	300mmHg
V.P. Equation:	$\text{Log}_{10}P(\text{mmHg})=7.80-1560/T(\text{K})$
Appearance:	Clear Liquid

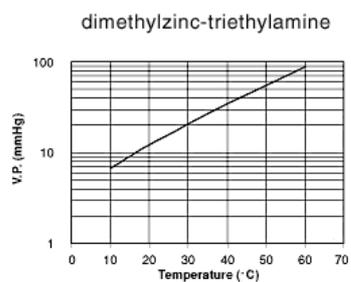


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Dimethylzinc-Triethylamine

DIMETHYLZINC-TRIETHYLAMINE PHYSICAL PROPERTIES	
Formula Weight:	196.4
Boiling Point @ (760mmHg):	95°C
Melting Point:	Not Available
Density @ 20°C:	Not Available
V.P. @ 20°C:	35mmHg
V.P. @ 40°C:	94mmHg
V.P. Equation: $\text{Log}_{10}P(\text{mmHg})=8.27-1970/T(\text{K})$	
Appearance:	Clear Liquid



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For the oxygen:

Oxygen
Alcohols
NO
NO₂
CO
CO₂
Others

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Algunas consideraciones

Los radicales ethyl tienen mucha menor reactividad comparado con los radicales Methyl.

Menor contaminación con Carbono para los radicales Ethyl

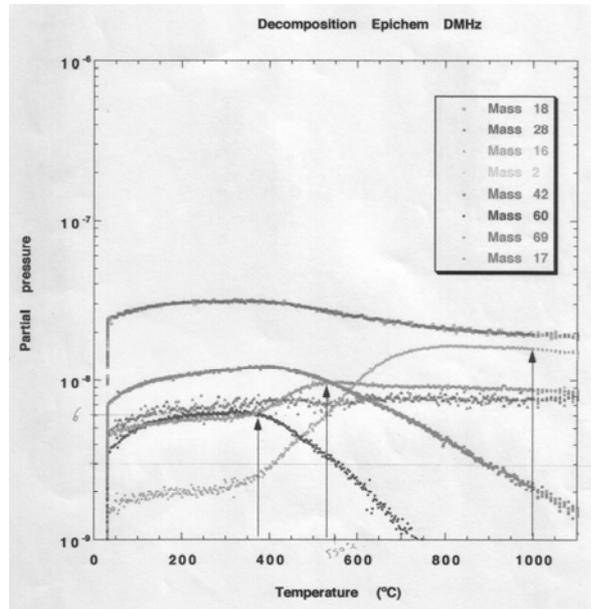
Un problema en el crecimiento del ZnO es la fuerte reactividad del Zn y el oxígeno.

Hay que evitar reacciones parásitas que pueden contaminar y deteriorar la capa.

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Estudio de la pirolisis de los precursores



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Metal-Organic Chemical Vapour Deposition

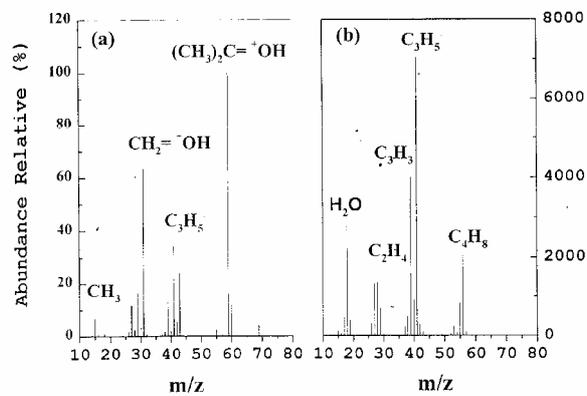
Spectrometer



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Pyrolysis data for tertiarybutanol



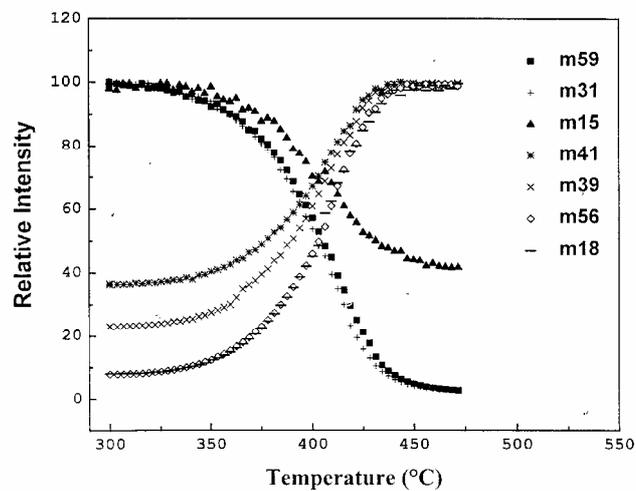
(a) Room temperature

(b) At 480 °C

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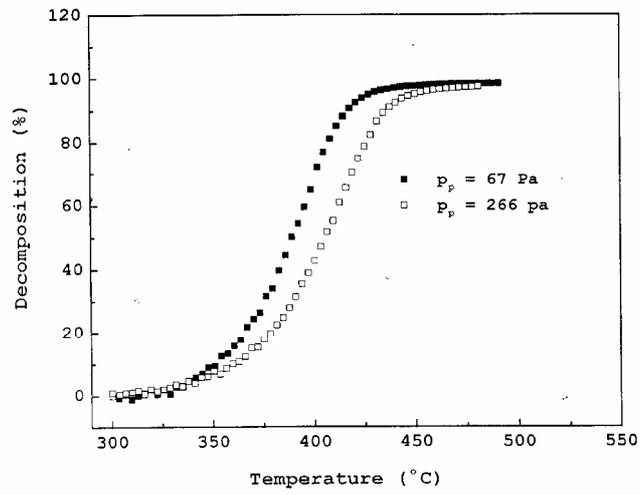
Decomposition of Tertiarybutanol



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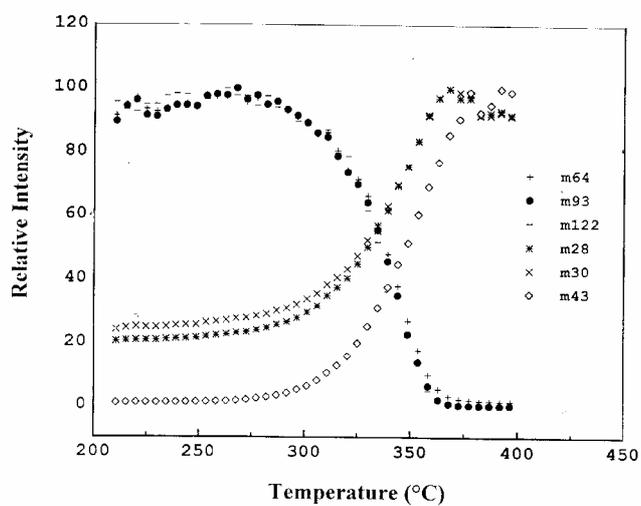
Decomposition of DEZn



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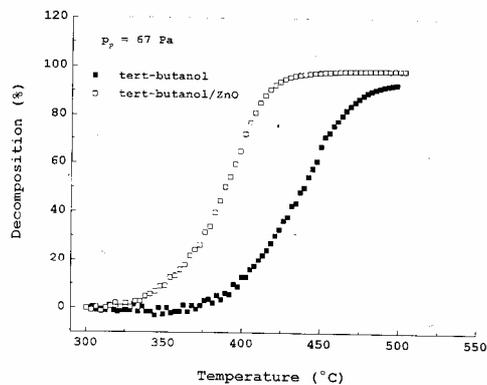
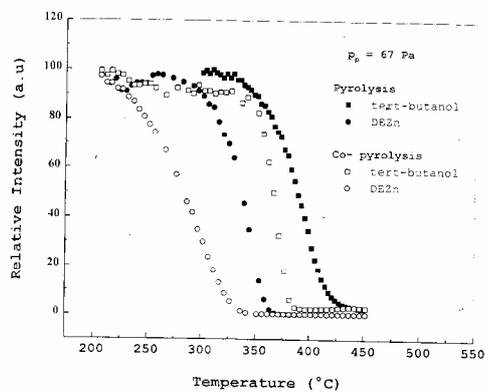
Co-pyrolysis of Tertiarybutanol and DEZn



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Comparison of co-pyrolysis and pyrolysis



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What substrate to use?

Sapphire
ZnO
MgO
Glass
Silica
Others

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Substratos para el GaN

Table 3.5 Lattice parameters and thermal coefficient of GaN and its substrates (after [176, 142, 121]).

Material	Lattice parameter a (Å)	Lattice parameter c (Å)	Thermal expansion coefficients (K^{-1})
GaN	3.189	5.185	$\alpha_a = 5.59 \times 10^{-6}$ $\alpha_c = 3.17 \times 10^{-6}$
Al ₂ O ₃	4.758	12.991	$\alpha_a = 7.5 \times 10^{-6}$ $\alpha_c = 8.5 \times 10^{-6}$
6H-SiC	3.08	15.12	$\alpha_a = 4.2 \times 10^{-6}$ $\alpha_c = 4.7 \times 10^{-6}$
3C-SiC	4.36	–	$\alpha = 2.7 \times 10^{-6}$
ZnO	3.252	5.213	$\alpha_a = 2.9 \times 10^{-6}$ $\alpha_c = 4.75 \times 10^{-6}$
GaAs	5.653	–	$\alpha = 6.0 \times 10^{-6}$
Si	5.43	–	$\alpha = 3.59 \times 10^{-6}$
LiGaO ₂	$a = 5.402, b = 6.372$	5.007	
MgAl ₂ O ₄	Spinel structure, mismatch with GaN using (111) surface: 9–10%		

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Sapphire as substrate

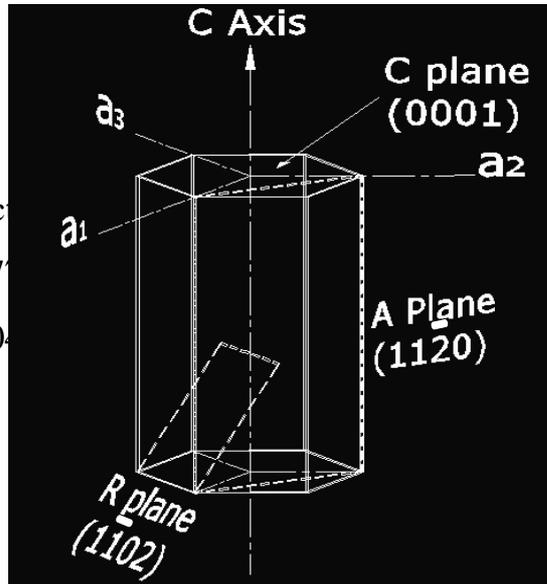
Crystallographic
planes: *Wurzite struc*

$C^a (0001) \bar{c} 4.7$

$R^c (11\bar{2}0) \bar{a}_1 13.0$

A (1 1 -2 0)

M (1 -1 0 0)



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Algunas consideraciones de carácter general

La baja temperatura es importante por razones técnicas

Efecto de tensiones en el calentamiento y enfriamiento

Concentración de defectos...

El crecimiento es tridimensional

Aparece una gran diferencia de parámetro de red con el
substrato mas utilizado:El zafiro

Una posibilidad sería la utilización de una capa de transición

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Velocidad de crecimiento

La velocidad de crecimiento puede ser controlada por dos tipos de mecanismos:

Reacciones superficiales. La velocidad de crecimiento crece exponencialmente con T. Proceso activado térmicamente

Proceso limitado por la llegada de los reactantes al substrato: En el rango de alta temperatura (sin descomposición del cristal) las reacciones químicas son suficientemente rápidas y la velocidad de crecimiento esta limitada por la llegada de los reactantes a la superficie. Estamos en el caso limitado por la difusión

El valor optimo depende de la fuerza de enlace del cristal, la estabilidad térmica, la química de los precursores.

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Velocidad de crecimiento

Caso del GaN

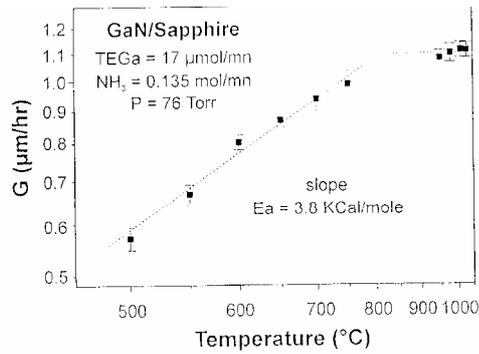


Fig. 3.1 Logarithm of the growth rate of GaN versus reciprocal temperature. Two regimes are evidenced: the kinetic mode at low growth temperature and the diffusion limited mode at high temperature.

Caso del ZnO

Table 1
 Experimental conditions for the ZnO MOCVD growth on sapphire

Temperature (°C)	Total flow (l/min)	T_{H_2} (Pa)	T_{O_2} (Pa)	Total pressure	Substrate position
270-450	5.5	14	30	atmospheric	3 cm from gas inlet

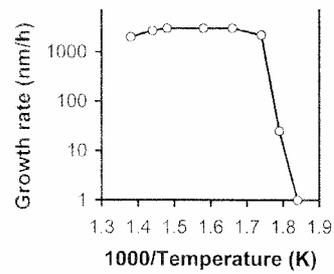


Fig. 4 Growth rate as a function of the susceptor temperature.

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Growth rate

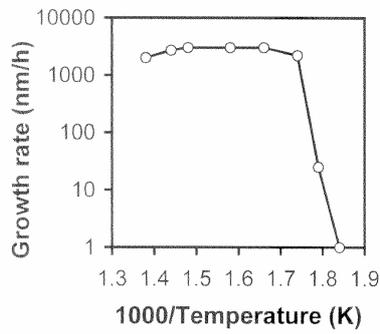
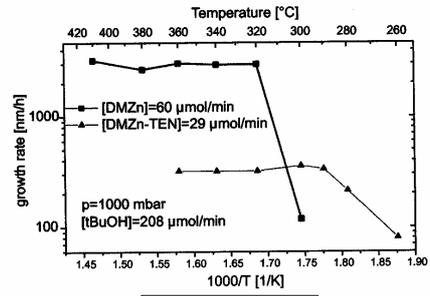


Fig. 1. Growth rate as a function of the susceptor temperature.



TH. GRUBER, et al.
 phys. stat. sol. (b) 229,
 No.2, 841-844 (2002)

Table 1
 Experimental conditions for the ZnO MOCVD growth on sapphire

Temperature (°C)	Total flow (l/min)	$P_{DE,Zn}$ (Pa)	P_{t-but} (Pa)	Total pressure	Substrate position
270-450	5.5	14	70	atmospheric	3 cm from gas inlet

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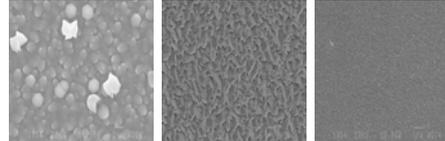


Algunos resultados de caracterización

FWHM muy ancha >300 Arcs.

Concentración de portadores alta (tipo n) 10^{19}

Morfologías muy variadas



Parece que los problemas vienen de un crecimiento tridimensional. Crecimiento de islas (Volmer-Weber)

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Control de la morfología: influencia de las condiciones de crecimiento

Densidad de la nucleación inicial

Cociente entre el crecimiento lateral y el vertical

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Control de la densidad de nucleación inicial

Temperatura

Presión parcial del precursor de Zinc: Altas presiones parciales provocan alta nucleación

Efecto de la presión en el reactor

Efecto del carrier gas y velocidad del mismo, lo que afecta al grosor de la capa de contacto

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Control de la nucleación inicial

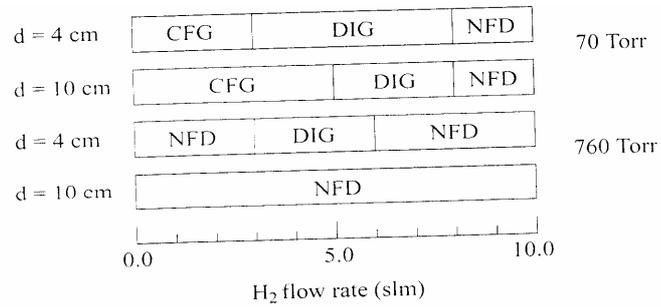


Fig. 3.2 Effect of the H_2 carrier gas flow rate on the GaN epilayers morphology, from [161].

A presión atmosférica no es posible crecer una capa continua debido a la baja densidad de nucleación inicial

Hay cierta controversia en el análisis, pero el efecto está ahí

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Control del crecimiento lateral

Effect of growth conditions on GaN epilayers morphologies.

Nucleation → ↓ Lateral growth	Low (high Tg, Low Ga)	High (low Tg, high Ga)
Low (low Tg, high Ga)	Discontinuous islands Hexagonal pyramids	Continuous films Hexagonal pyramids
High (high Tg, low Ga)	Discontinuous islands Flat-top pyramids	Continuous films Flat-top pyramids

La condición para mejorar la nucleación inicial y la condición para promover el crecimiento lateral son contrapuestas.

No parece posible obtener excelentes films creciendo directamente sobre el sustrato

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Crecimiento usando una capa buffer El caso de GaN

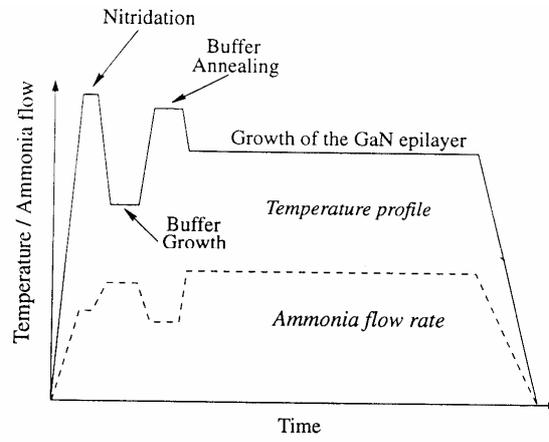
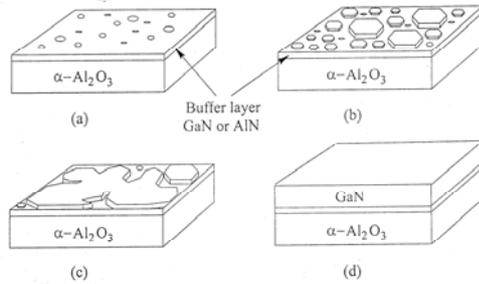


Fig. 3.3 Sketch of the double-step process: temperature and precursors flow versus time.

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Efecto de la capa buffer: caso del GaN



Mechanism of hexagonal islands coalescence, leading to 2D growth for GaN grown on a buffer layer.

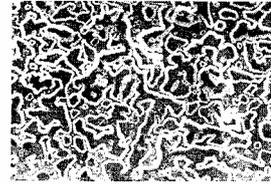


Fig. 3.5 SEM picture taken during the coalescence stage of the hexagonal GaN islands.

Debido a la baja energía interfacial se obtiene una alta densidad de nucleación.

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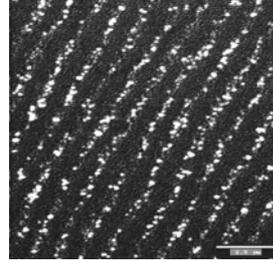
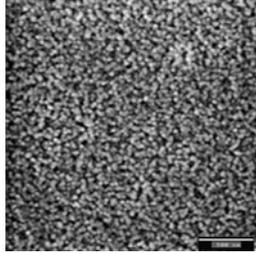


Capas buffer de ZnO

Orientación C

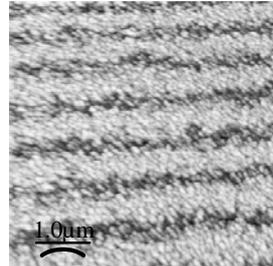
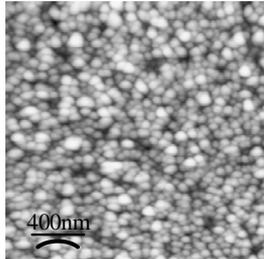
Orientación R

SEM



Buffer
T=350
R=10
<(25)
(30)>

AFM

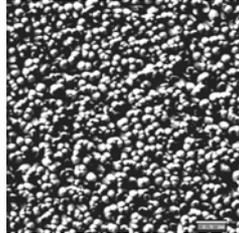


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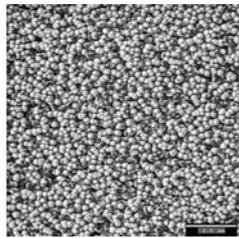


SEM

Orientación C

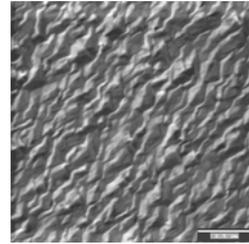
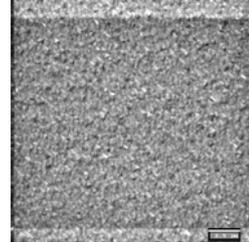


Crecimiento
Directo a
 $T=400$
 $\langle(22)$
 $(6)\rangle$



Crecimiento
Con buffer a
 $T = 350$,
Crecimiento a
 $T=400$
 $\langle(28) (18)\rangle$

Orientación R



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Efecto de la capa buffer sobre los parámetros del crecimiento

¿Por qué baja temperatura?

Se produce un depósito más uniforme como consecuencia de la alta supersaturación de las especies en el sustrato y las bajas movilidades. Por supuesto, la calidad cristalina es mala

El grosor óptimo de la capa buffer no está determinado a priori. Experiencias de reflectividad.

Idéntico comentario para la ratio entre los precursores: no necesariamente la misma que para el crecimiento

Puede ser interesante un annealing pre-growth

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Caso del GaN

Efecto de la Nitridación.

Efecto del grosor de la capa buffer

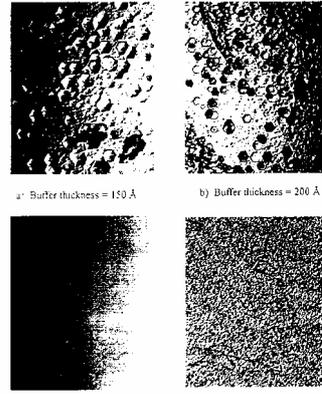
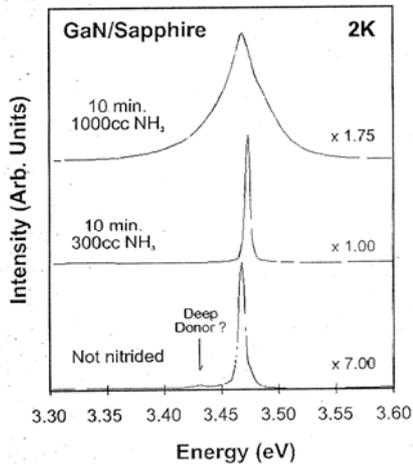


Fig. 3.7 GaN surface morphology versus GaN buffer layer thickness.

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Caso del GaN

Efecto de la relación entre los precursores

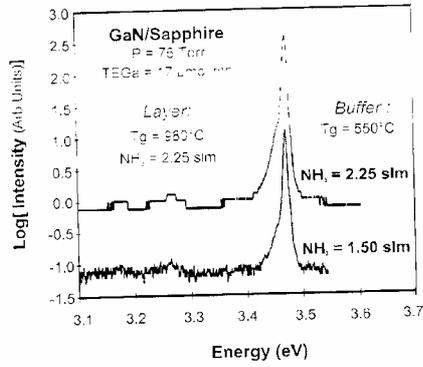
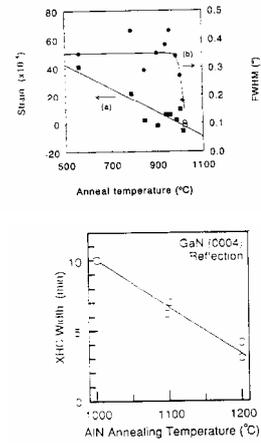


Fig. 3.8 2K photoluminescence versus buffer V/III molar ratio. The lineshape is the same but the intensities differ greatly.

Efecto del recocido antes del crecimiento

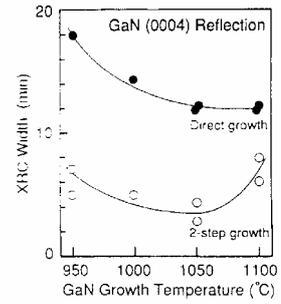
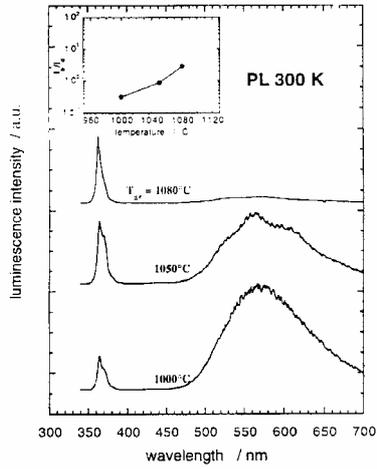


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Influencia de los parámetros de crecimiento

Efecto de la temperatura de crecimiento GaN



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Influencia de los parámetros de crecimiento



PERGAMON

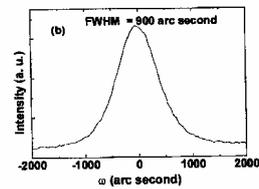
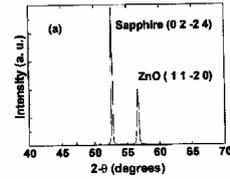
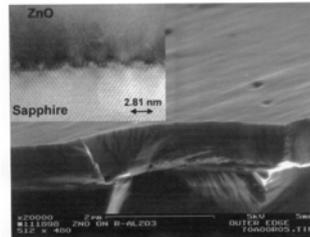
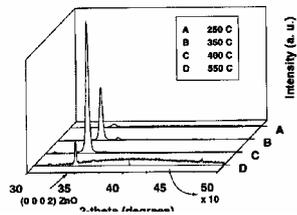
Materials Science in Semiconductor Processing 2 (1999) 247-252

MATERIALS
SCIENCE IN
SEMICONDUCTOR
PROCESSING

Epitaxial ZnO piezoelectric thin films for saw filters

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Thin Solid Films 402 (2002) 302–306



Photoluminescence and structure of ZnO films deposited on Si substrates by metal-organic chemical vapor deposition

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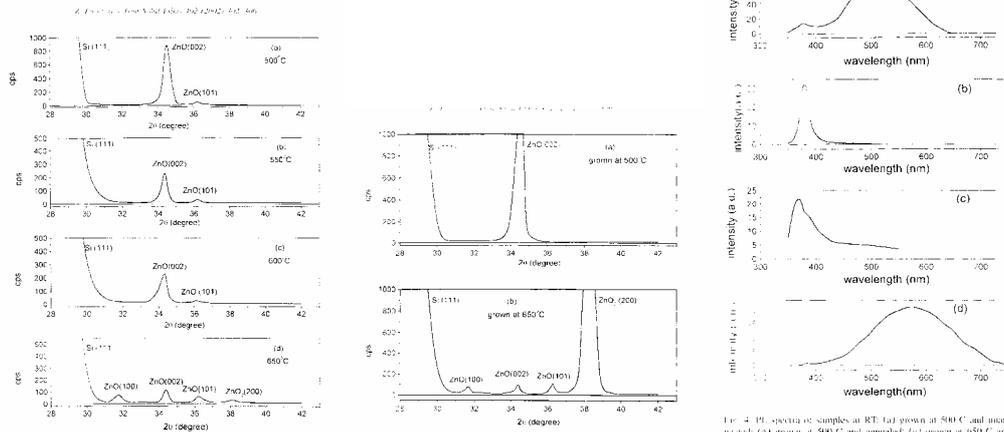
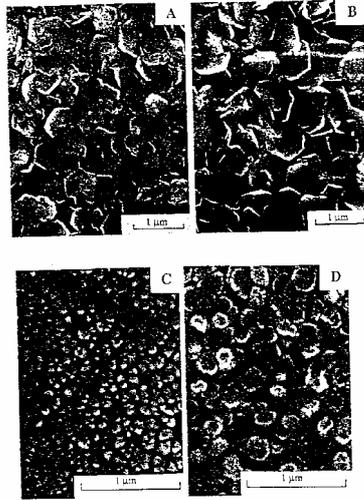


Fig. 2. XRD patterns of the samples grown at 500, 550, 600 and 650°C, respectively. (a)–(d) XRD patterns and (e)–(h) PL spectra of the samples grown at 500°C (a), 550°C (b), 600°C (c) and 650°C (d) and annealed (e)–(h).

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Dependencia de la morfología
con la temperatura de
crecimiento

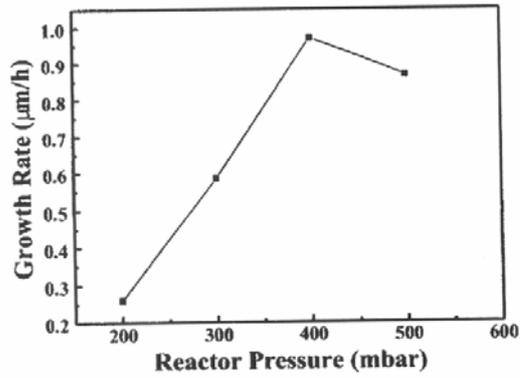
SEM

FIG. 4. Scanning electron micrographs of undoped ZnO films deposited at (a) 367 °C and (b) at 420 °C from 0.05% DEZ and 3.0% ethanol. The aluminum-doped films deposited at 367 and 420 °C from 0.05% DEZ, 0.03% TEA, and 3.0% ethanol are shown in (c) and (d).

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Efecto de la presión del reactor sobre la velocidad de crecimiento



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Efecto de la capa buffer

Fig.2. 0-20 scans of ZnO grown on GaN template (a), c-plane sapphire (b), and ZnO substrate (c)
Fig.3. PL spectra at 5 K of ZnO grown on ZnO substrate (a), GaN template (b), and c-plane sapphire (c)

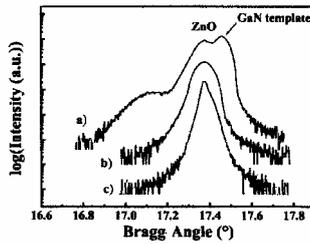


Fig. 2

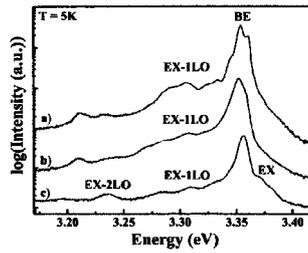


Fig. 3

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Textured aluminum-doped zinc oxide thin films from atmospheric pressure chemical-vapor deposition

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 (Received 27 August 1991; accepted for publication 4 October 1991)

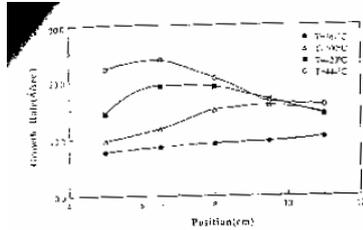


FIG. 1. Growth rate profile as a function of deposition temperature. The reactant gas mixture contains 0.05% DEZ, 0.03% TEA, and 3.0% ethanol.

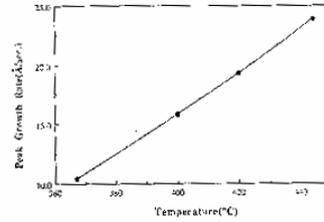


FIG. 2. Peak growth rate dependence on deposition temperature. The samples were the same as in Fig. 1.

Velocidad de crecimiento en función de diferentes parámetros

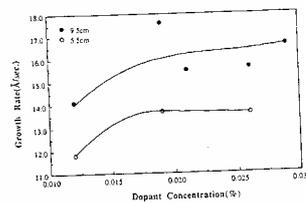


FIG. 3. Dependence of growth rates at a position 5.5 and 9.5 cm from the reactor nozzle on dopant concentrations. The films were deposited at 400°C from 0.05% DEZ and 3.0% ethanol.

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Efecto de la ratio

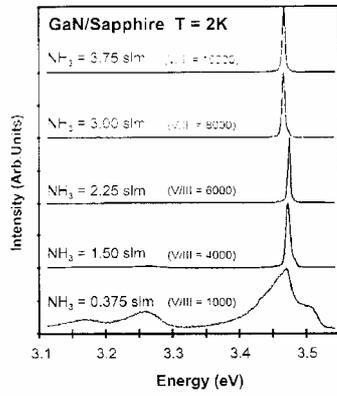


Fig. 3.14 2K photoluminescence of GaN versus V/III molar ratio.

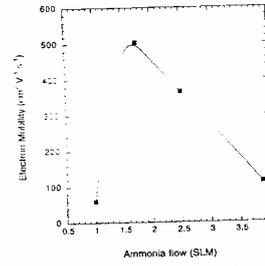


Fig. 3.13 Mobility of GaN versus V/III molar ratio [37].

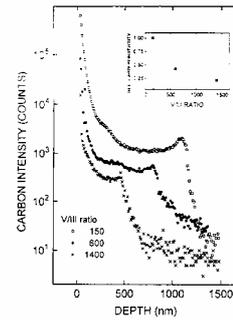


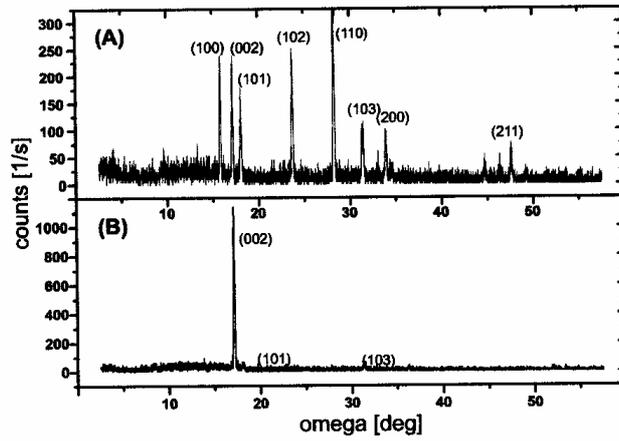
Fig. 3.15 SIMS analysis of carbon in GaN versus V/III molar ratio (from [143])

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Efecto de la ratio

Figure 4. X-ray diffraction spectra of ZnO (A) grown with VI/II = 3.5 and (B) VI/II = 16 at 360 °C.

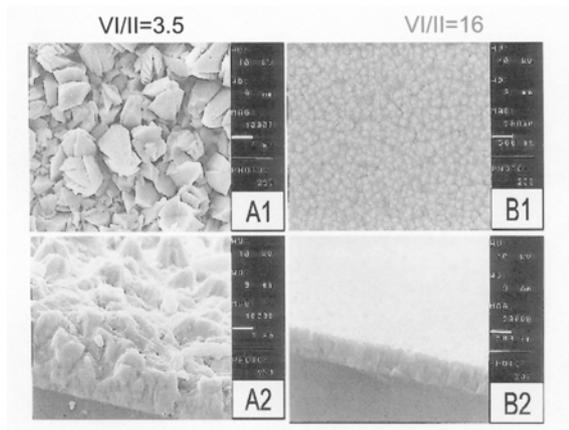


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SEM images of ZnO layers grown (A) with VI/II = 3.5 and (B) VI/II = 16 at 360 oC.



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Efecto de la ratio entre los precursores

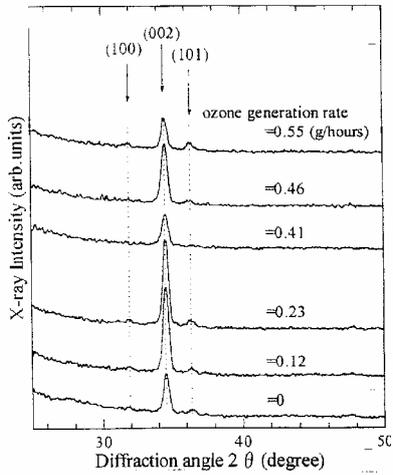


Fig. 3. X-ray diffraction pattern of the films deposited at different ozone generation rate.



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Preparation of ZnO films by atmospheric pressure chemical-vapor deposition using zinc acetylacetonate and ozone

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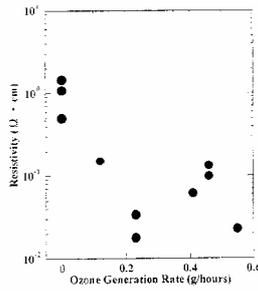


Fig. 4. Resistivity of a function of the ozone generation rate.

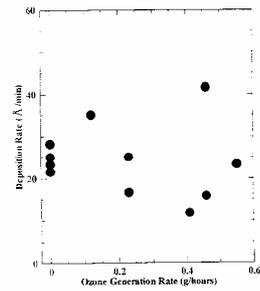


Fig. 5. Deposition rate of the films as a function of the ozone generation rate.

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