Laboratoire des Science des Procédés et des Matériaux
LSPM-CNRS UPR 3407 (ex. LIMHP)
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Procédé d'élaboration Spray plasma pour électrode Photovoltaïque

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- ZnO et le photovoltaïque
- Procédé Spray Plasma
- Caractéristiques des couches minces de ZnO.
- Influence des paramètres opératoires sur les dépôts.
- Conclusion

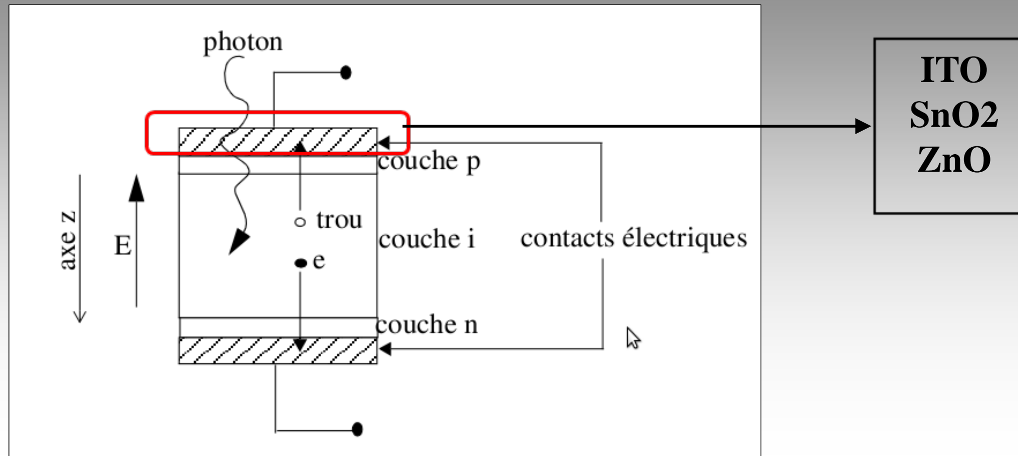


Fig.1. Structure de base d'une cellule photovoltaïque à base Si

- Le ZnO est un semi-conducteur de large gap (3,6 eV).

- Une impotente transmittance de plus de 80% dans la région du visible (380-900 nm) ,

-Une conductivité élevée (10 - $5.10^{3}\ \Omega^{-1}.cm^{-1}$).

- Non toxique et abondant

Procédé Spray Plasma

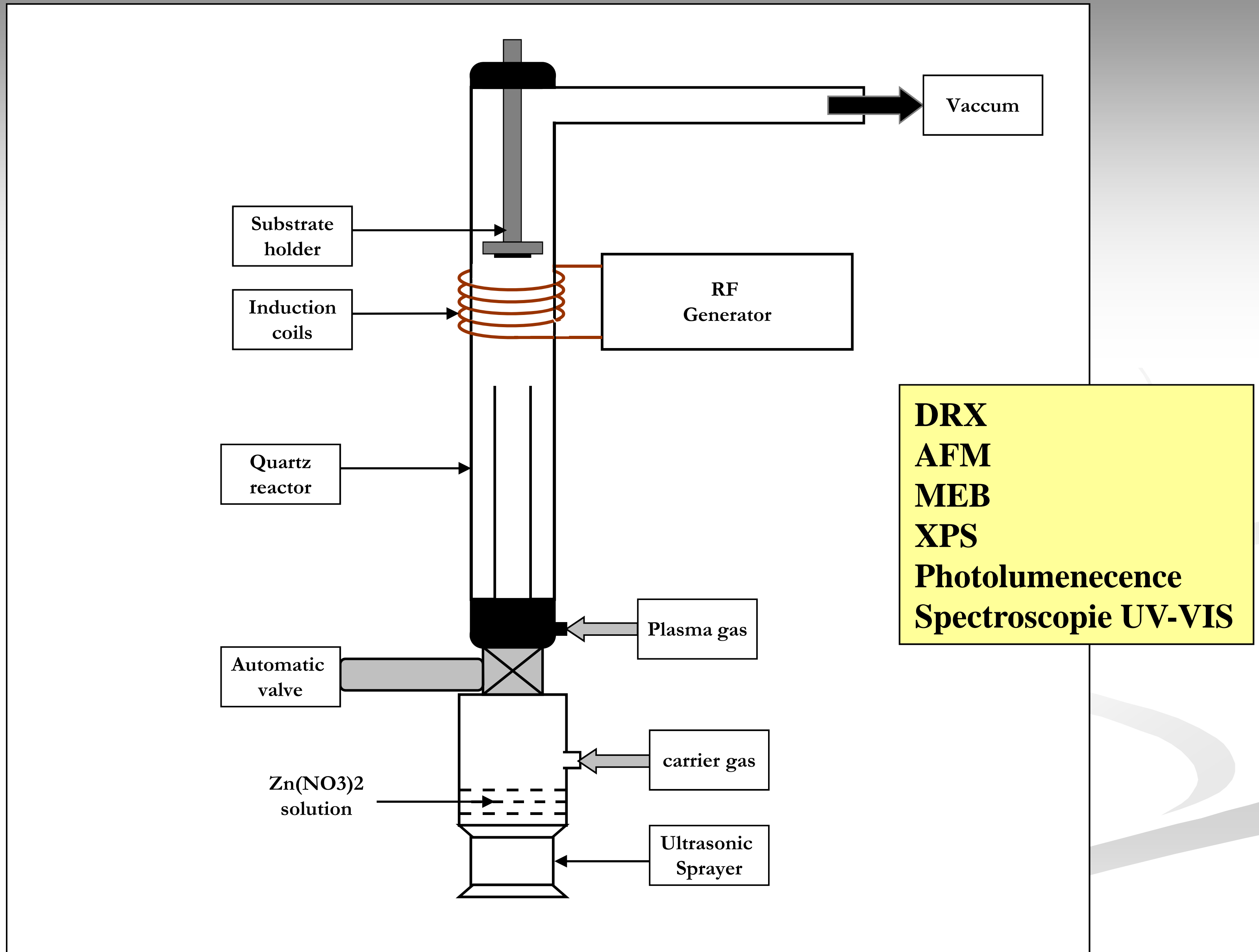


Fig.2 . Experimental set up

DRX
AFM
MEB
XPS
Photolumenecence
Spectroscopie UV-VIS

Caractéristiques des couches minces de ZnO déposées par Spray plasma

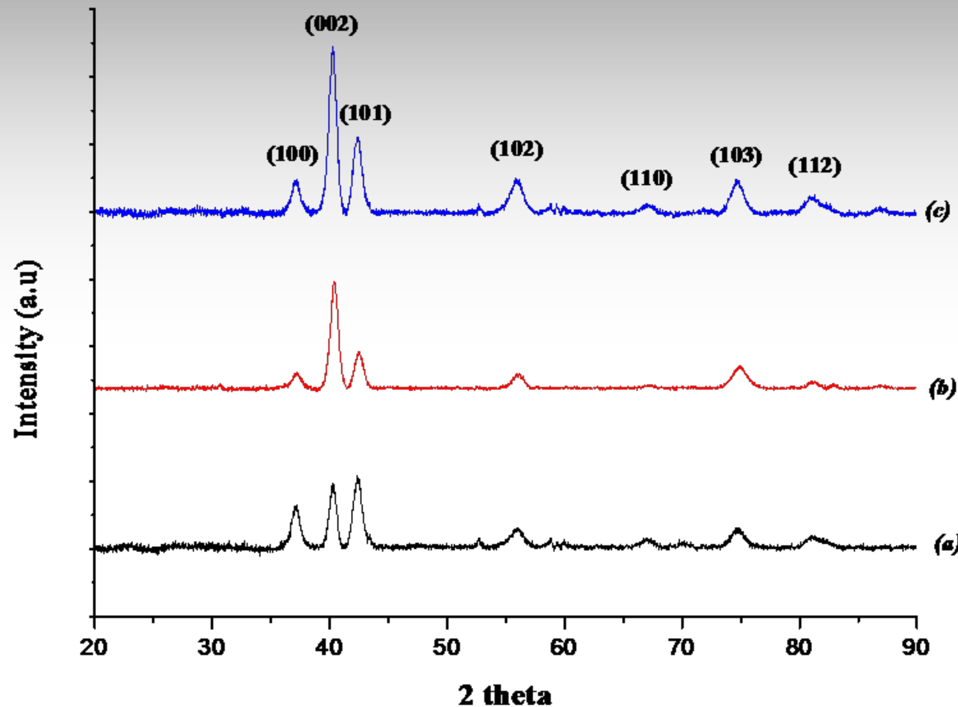


Fig.3 . XRD patterns of Al-ZnO prepared at various Plasma gas composition

Sample	Cristalyte size (nm)	Strain
(a)	33	0,005
(b)	100	0,006
(c)	14	0,002

Table.1 . Cristalyte size and strain using Williamson Hall plot[1] as fonction of plasma gas composition

$$\beta \cos\theta = k\lambda / T + 4\,\varepsilon \sin\theta$$

(a) $(Ar:O_2)$ = (200:10)mL/min
(b) $(Ar:O_2)$ = (200:0)mL/min
(c) $(Ar:O_2)$ = (100:0)mL/min

1. G.K. Williamson, H.Hall, ActaMetall. 1(1953)22–31.

Caractéristiques optiques des couches

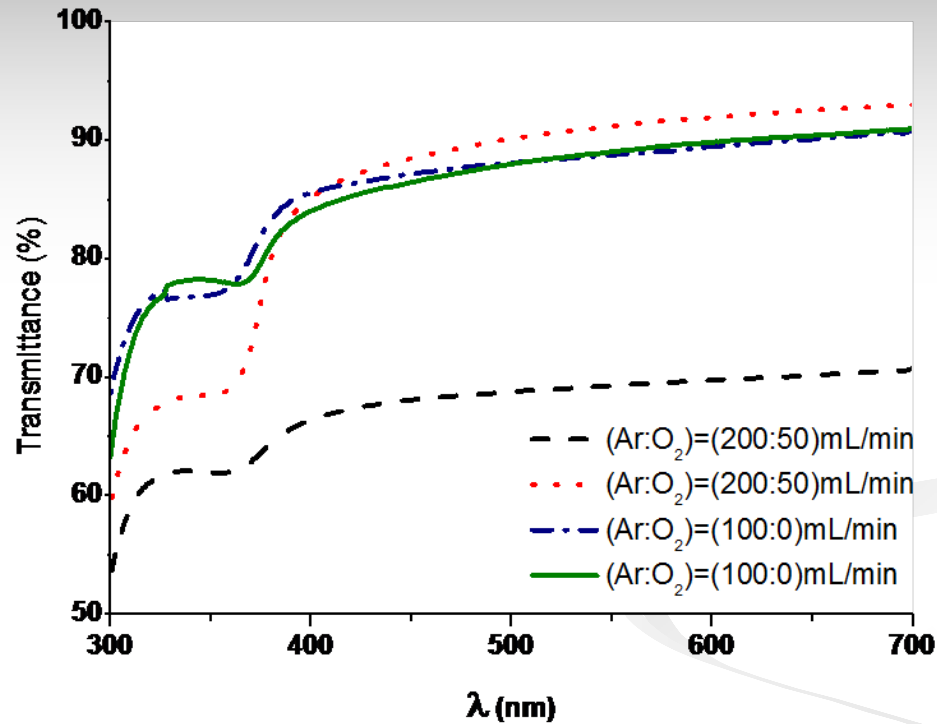


Fig. 4. Transmission spectra of the ZnO films for different plasma gaz composition C=0.1M; Substrate temperature =200°C; anealing temperature= 400°C

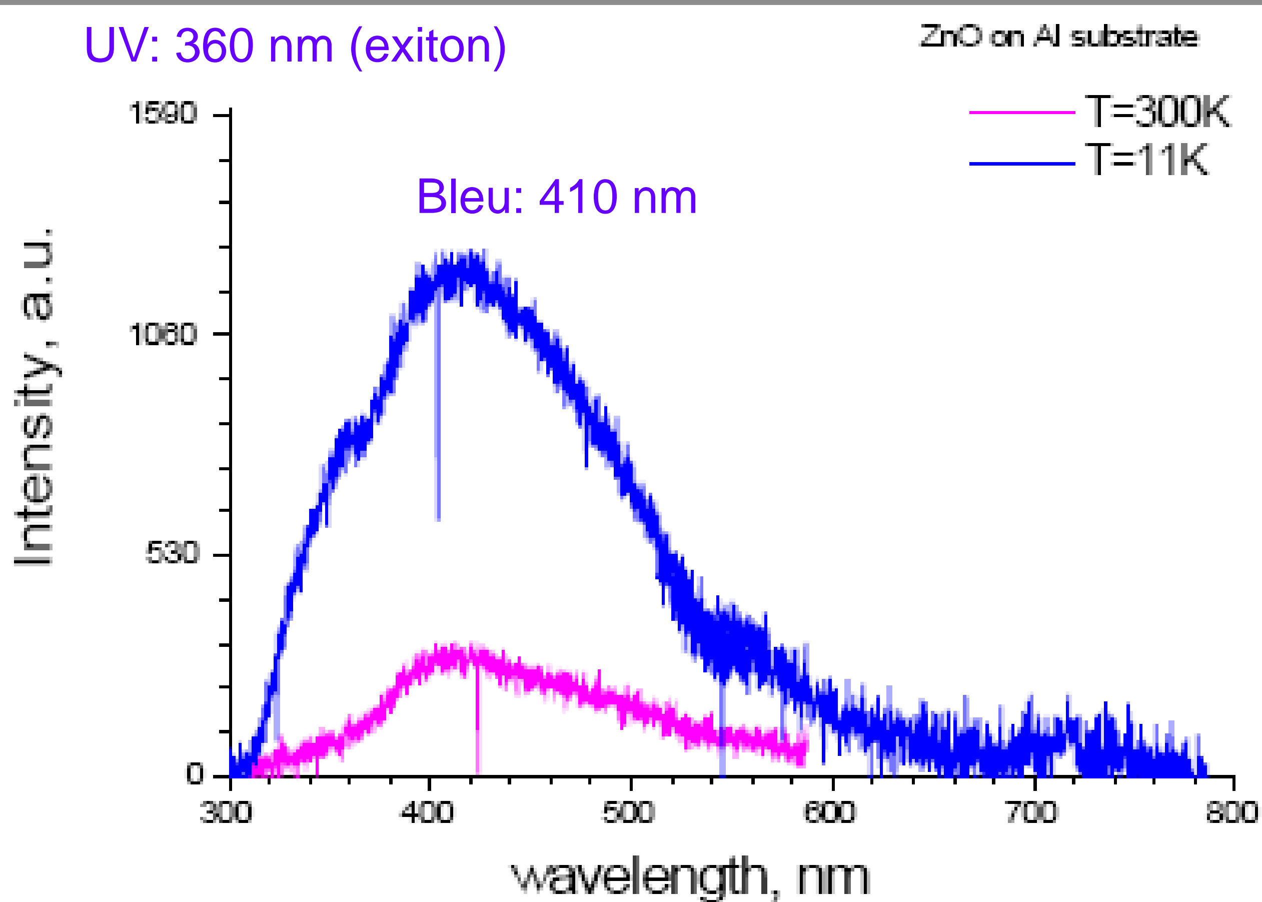


Fig.5 . Photoluminescence of ZnO thin film deposited on aluminum substrate. Fluorescence spectroscopy performed in ultra vacuum (<10-9 mbar) and cryogenic temperature (11K).
C=0.1M; (Ar:O2)=(200:50)mL/min; anealing temperature= 400°C

Superlumi experimental station (HASYLAB at DESY)

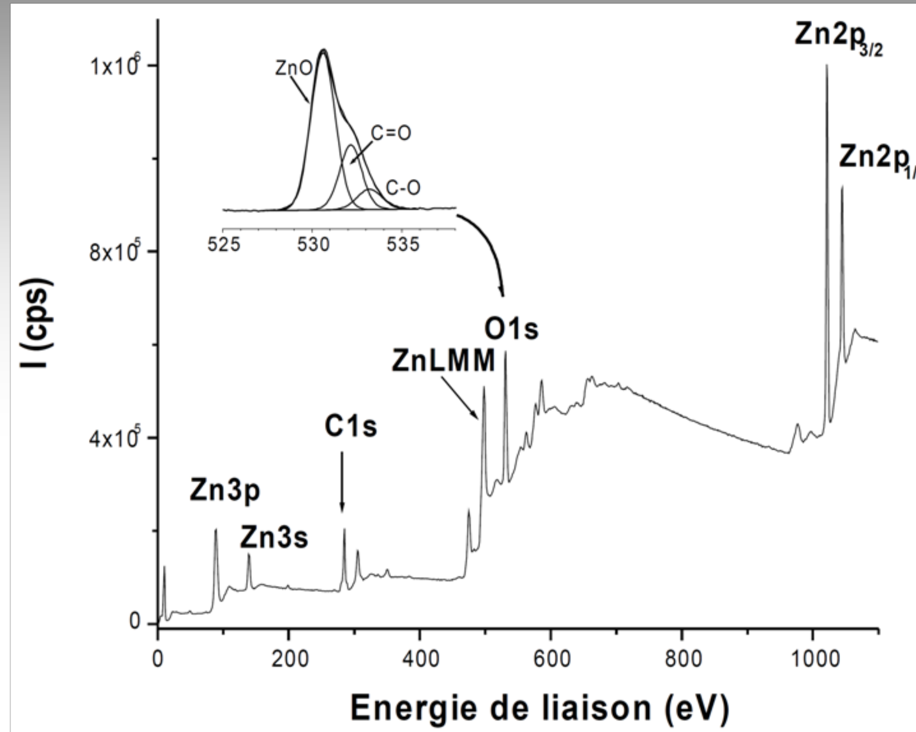


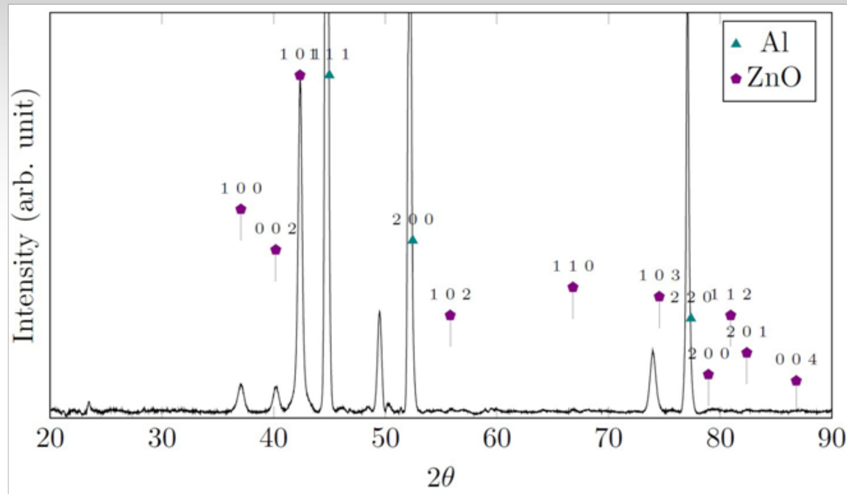
Fig.6 . XPS spectra of ZnO thin film

Table 2. Chemical composition of ZnO Suface layer by XPS

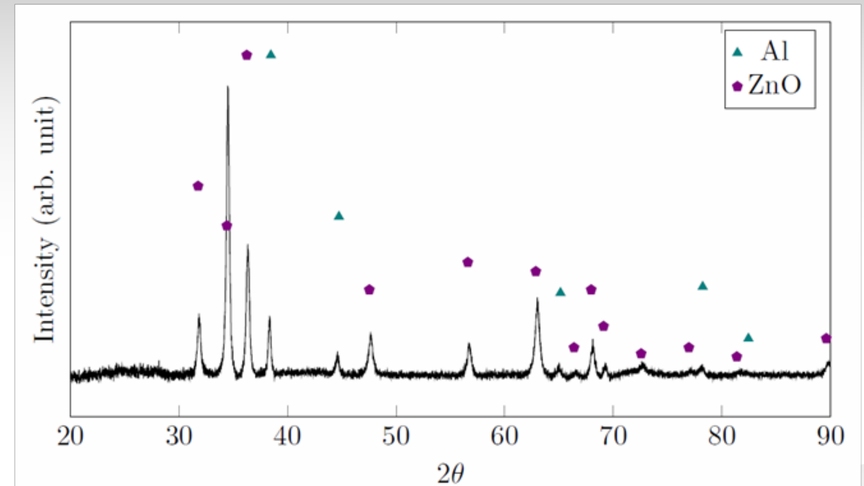
Element	Raie	Postion (eV)	LMH (eV)	at. %
Zn	Zn2p3	1021.7	1.86	24.72
C	C1s	285.0	1.53	35.40
O	O1s (ZnO)	530.6	1.61	26.46
	O1s (C=O)	532.2	1.50	9.99
	O1s (C-O)	533.2	1.62	3.44

Zn/O = 0,93

Influence du substrat sur les dépôts

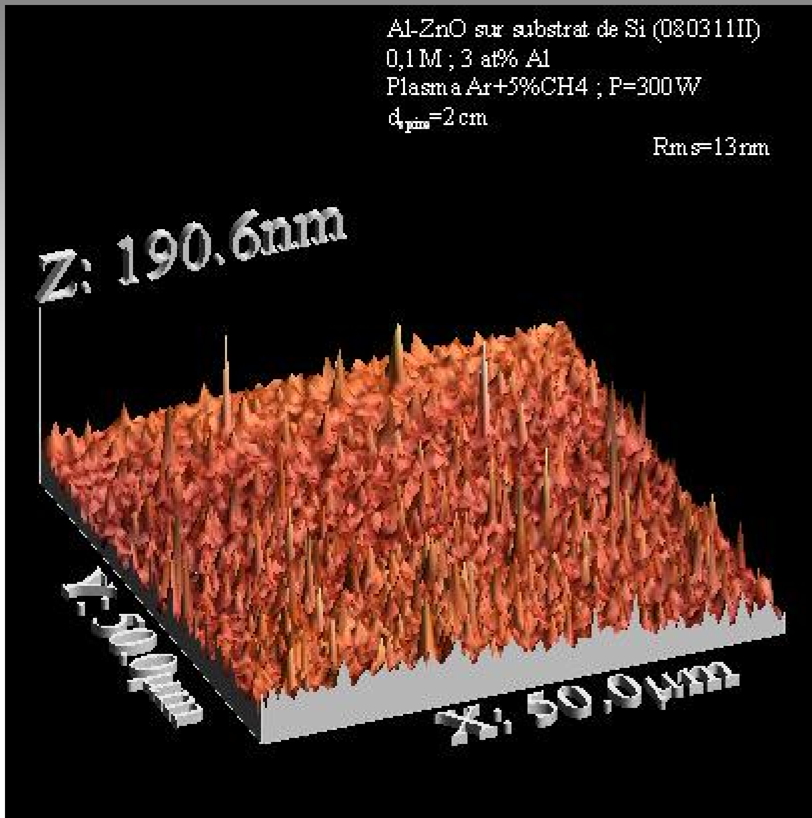


(a)

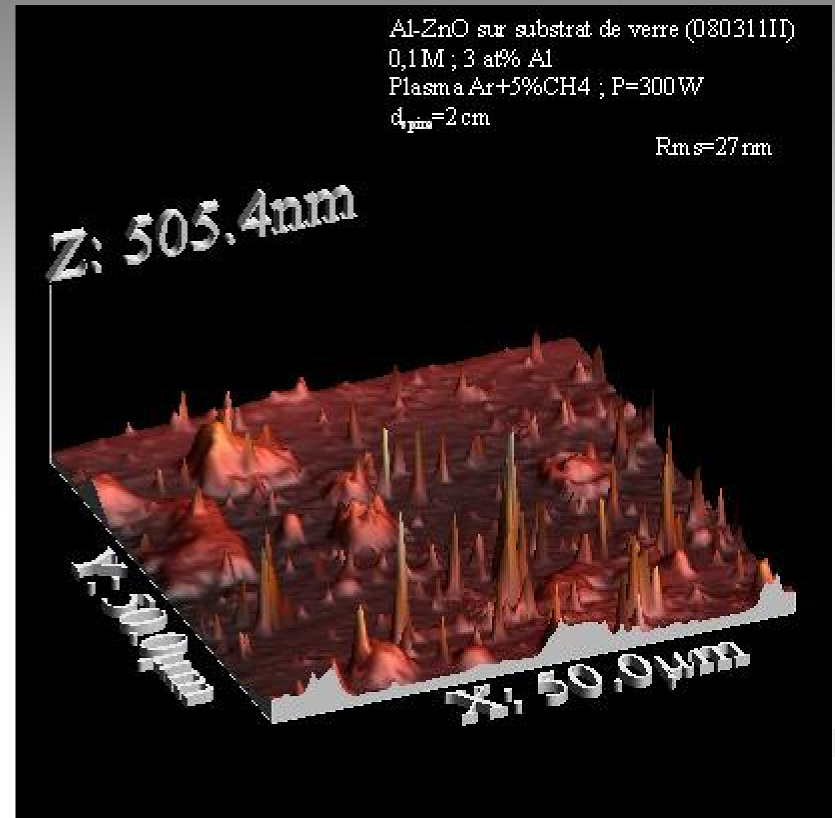


(b)

Fig. 7 . XRD patterns of Al-ZnO deposited on (a) aluminium substrate and (b) glass substrate C=0.1M, 3 *at* % Al; Substrate temperature =200°C; anealing temperature= 400°C



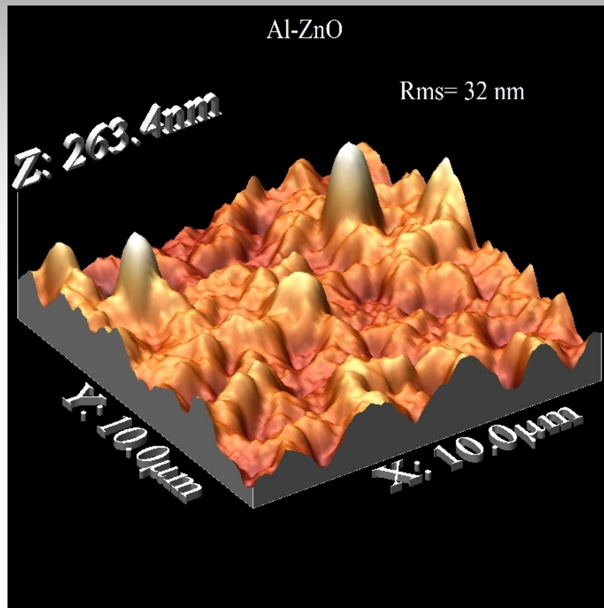
(a)



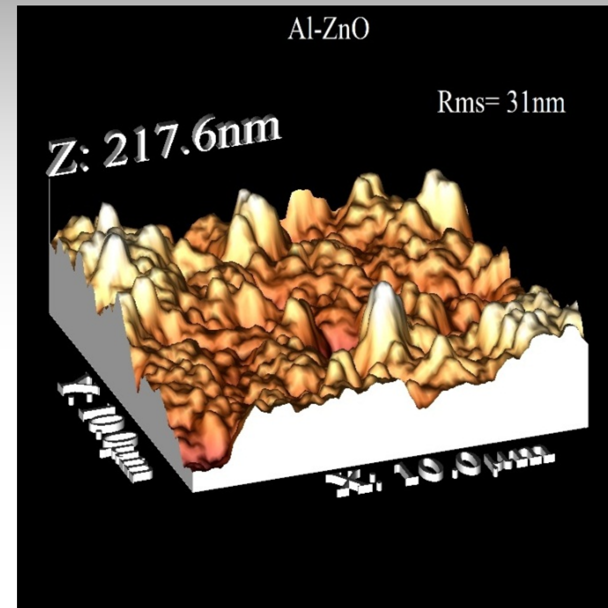
(b)

Fig.8 . AFM image of Al-ZnO films deposited on glass and Si substrate
(a) Si substrate, (b) glass substrate
C=0.1M, 3 wt% Al; Ar+CH4 plasma gas

Influence des gaz plasma sur les couches minces de Al-ZnO



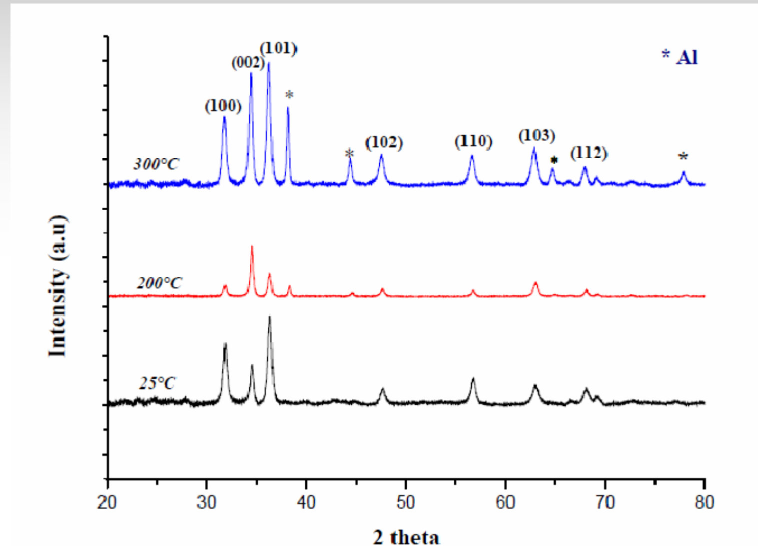
(a)

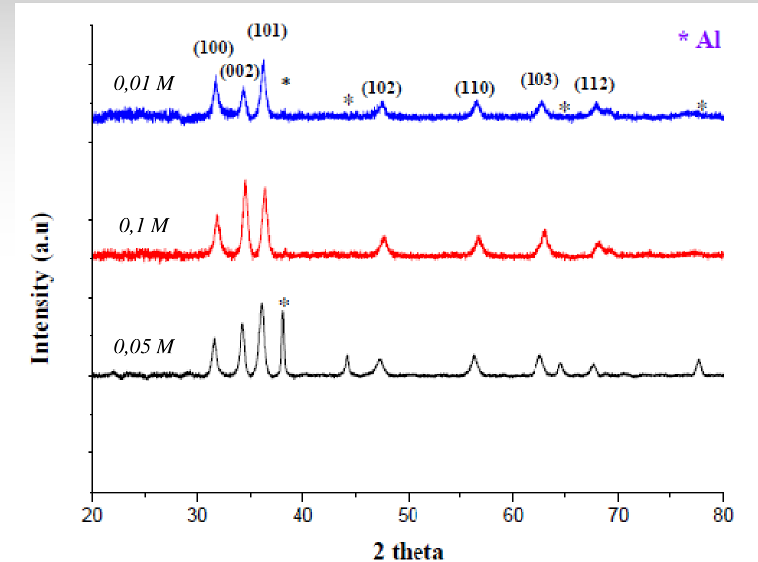


(b)

Fig.9 . AFM image of Al-ZnO films deposited on glass substrate
C=0.1M; Substrate temperature =200°C; anealing temperature= 400°C; 150 W
(a) (Ar:O2)=(200:10)mL/min (b) (Ar:O2)=(200:0)mL/min

Influence de la température du substrat et la concentration





T (°C)	T(nm)	ε
25	26	0.0005
200	33	0.0001
300	37	0.0016

C (mol/L)	T(nm)	ε
0.01	37	0.0020
0.05	36	0.0022
0.1	20	0.0005

(a) **(b)**

Fig.10 . XRD and cristalyt size ZnO thin film as fonction as (a) substrate temperature, (b) solution precursor concentration

Influence des la puissance plasma sur les couches minces de Al-ZnO

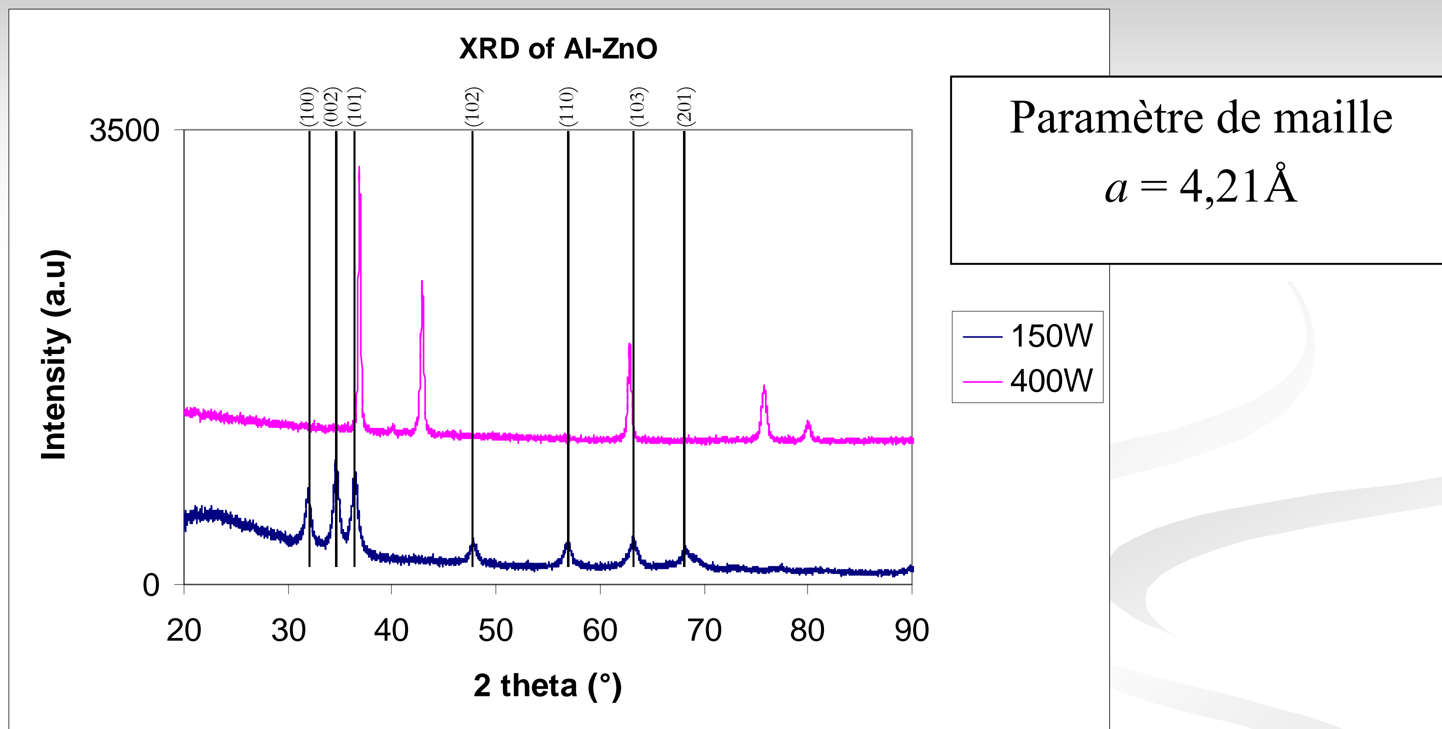
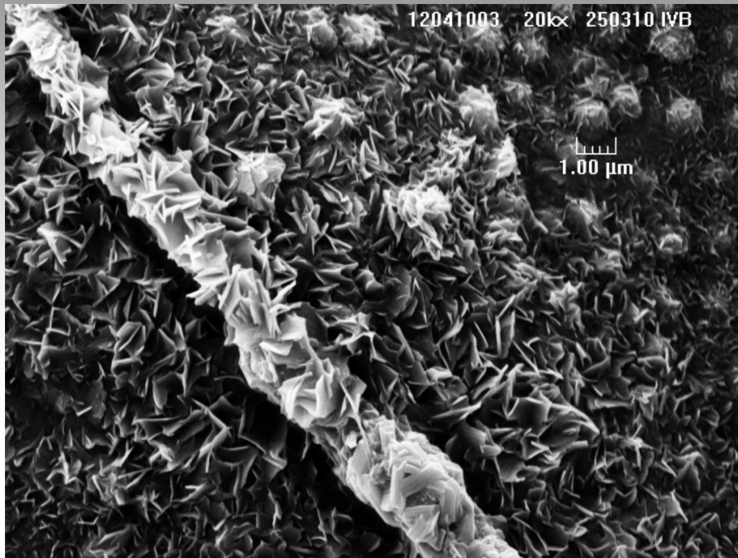
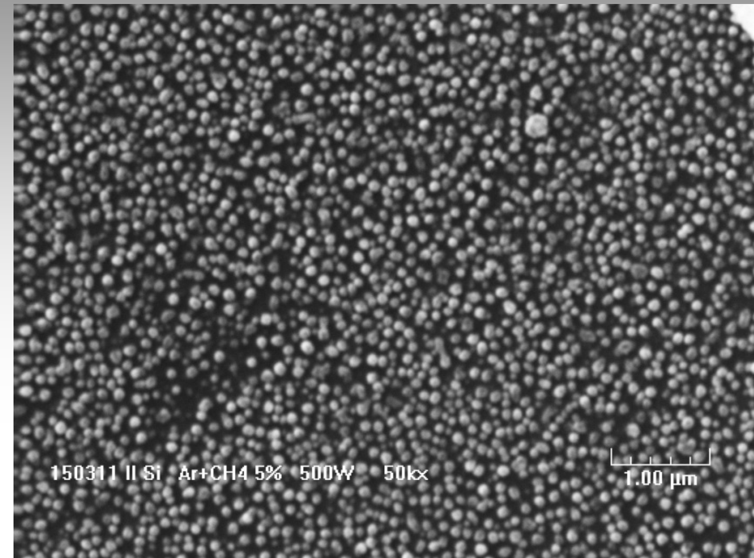


Fig.11 . XRD of Al-ZnO thin film deposited at plasma power of 150W and 400W. C=0.1M 3 at% Al; Ar+O2 plasma gas



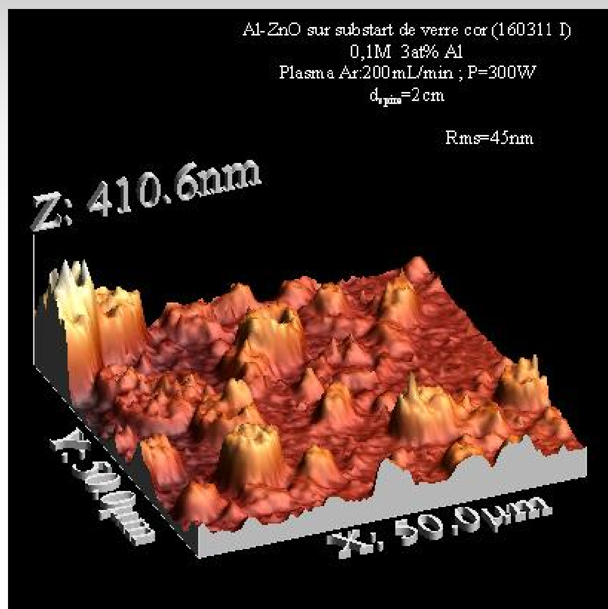
(a)

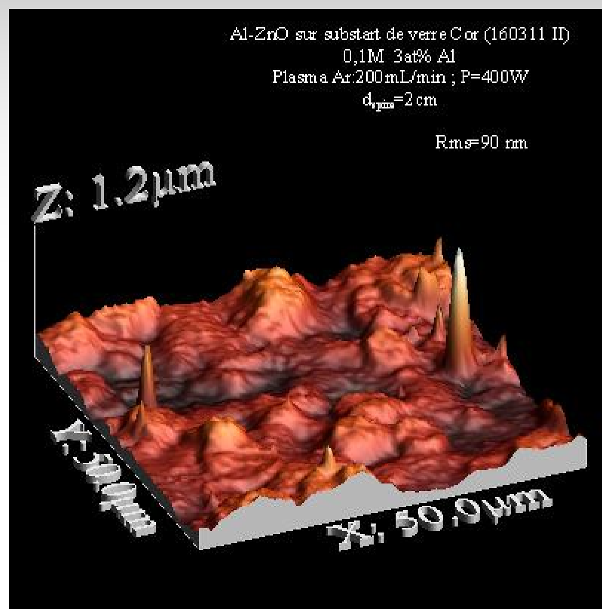


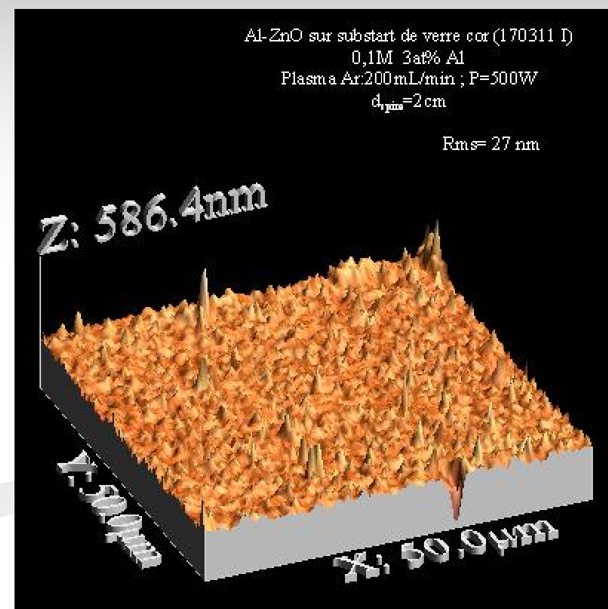
(b)

Fig.12 . ASM image of Al-ZnO films deposited at (a) 150W and (b) 500W plasma power

Influence des la puissance plasma sur les couches minces de Al-ZnO







300W **400W** **500W**

Fig.13 . AFM image of Al-ZnO as function as plasma power.
C=0.1M, 3 at% Al; glass substrate, Ar plasma gas

Conclusion

- Les couches minces de ZnO et Al-ZnO ont une structure de type hexagonal wurtzit
- L'orientation des couches peut être contrôlée par le contrôle de la température du substrat et la concentration
- Les images AFM et MEB montrent des couches rugueuse et fortement texturées (Rms = 5-50nm)
- Transmittance 80-90% dans le domaine du visible.

Remerciements au programme PIE CNRS

Merci de votre attention

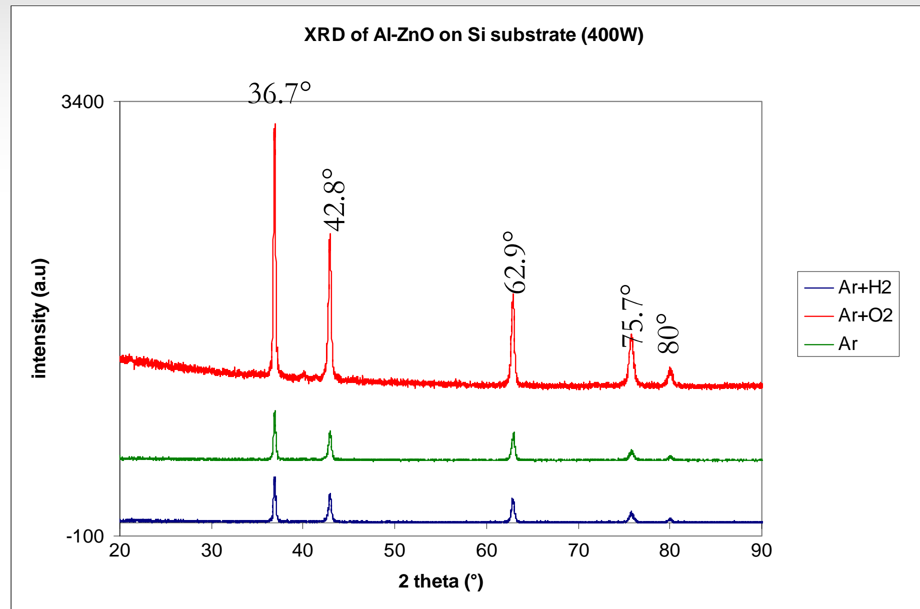
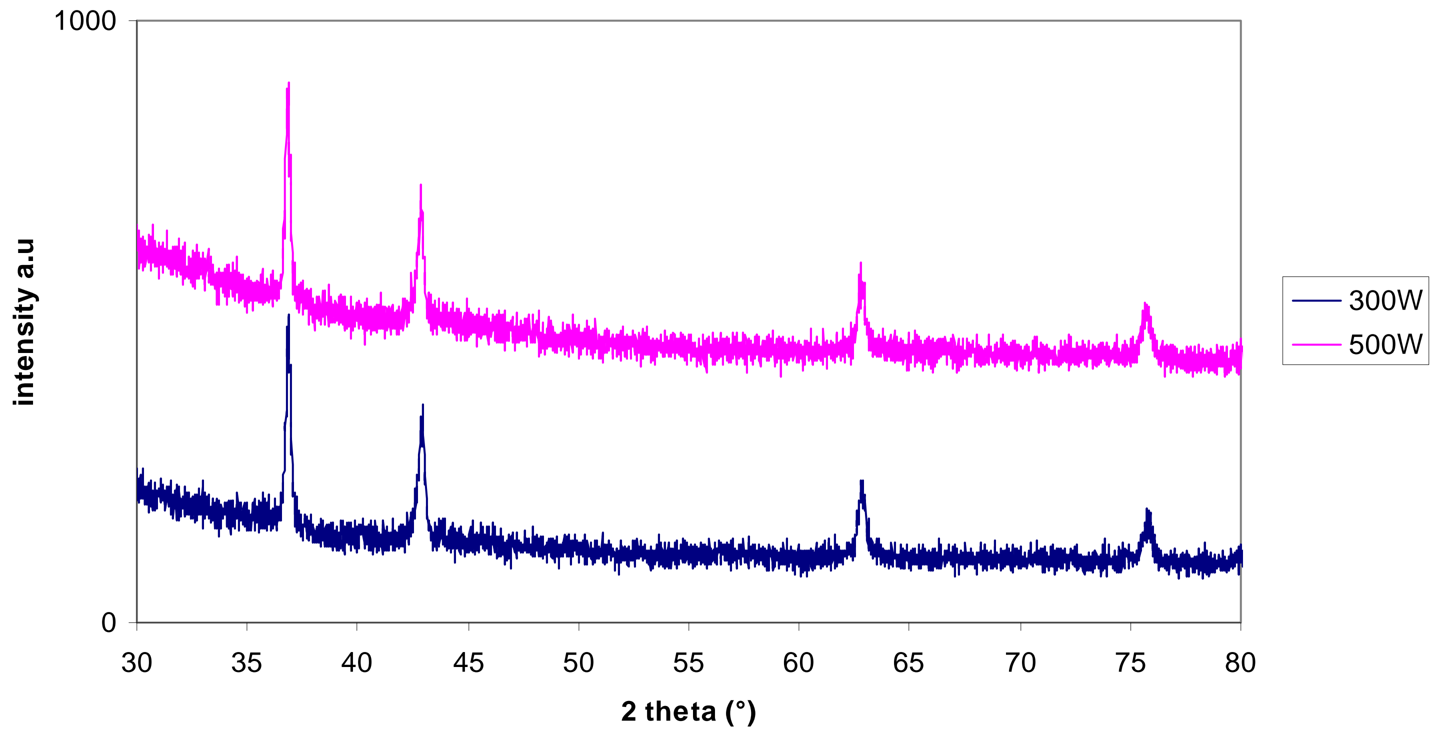


Fig.14 . XRD of Al-ZnO thin film deposited on Si and glass substrate (CuKα)


XRD of Al-ZnO on glass substrate and Ar+H2 plasma gas
1000
0
intensity a.u
30
35
40
45
50
55
60
65
70
75
80
2 theta (°)
300W
500W