Room Temperature Roll-to-Roll Deposition of ITO at the Center for Advanced Microelectronics Manufacturing

James C Switzer III, Mark D. Poliks, Paul Wickboldt, Elizabeth Tiberio, Mingming Guo

Introduction:

The Center for Advanced Microelectronics Manufacturing (CAMM) is a roll to roll flexible electronics research facility located at Binghamton University [1]. As part of the research needs of the CAMM and its member companies a method of depositing high quality Indium Tin Oxide (ITO) films onto polymer webs has been developed. High quality ITO thin films have a desirable combination of high conductivity and high optical transmission in the visible spectrum. ITO thin films are widely used in the electronics industry as a transparent conducting oxide (TCO's) in active matrix backplanes, solar cells and OLED lighting. ITO thin films have been deposited in the past on roll-to-roll sputter deposition tools with properties suitable for solar cells, organic lighting, touchscreen and OLED's [2,3]. In this paper we present ITO thin films deposited on PEN substrates that have properties that meet or exceed those reported in the literature [2,3].

Experimental:

ITO thin films were deposited onto 5 mil Teonex Q65FA PEN using the CHA Industries High Vacuum Coater (CHA) [4]. The CHA is a diffusion pumped roll-to-roll sputter deposition tool. (See figure 1 for coating layout design) Each target in the CHA is powered by two 10kW Pinnacle Plus+ pulsed DC power supplies. ITO thin films were deposited from a 90/10 In_2O_3/SnO_2 ceramic target with a matrix of O_2 flow and deposition pressure to investigate effects of each on ITO film properties. Following deposition films were annealed at 110° C in an atmospheric oven to further improve the film quality. Film thickness values were measured in a Phase-Modulated Spectroscopic Ellipsometer from Horiba Jobin Yvon. Film crystallinity was measured in a PANalytical's X'Pert Pro Materials Research Diffractometer. The glancing scan technique was used and an angle of 0.7 degrees was used for all films. A Filmetrics F-20 UV-Vis spectrophotometer was used to measure the transmission of the ITO films and and the PEN substrate. Sheet resistance measurements were made with a Jandel RM3-AR source measure unit fitted with a handheld 4-point probe unit.

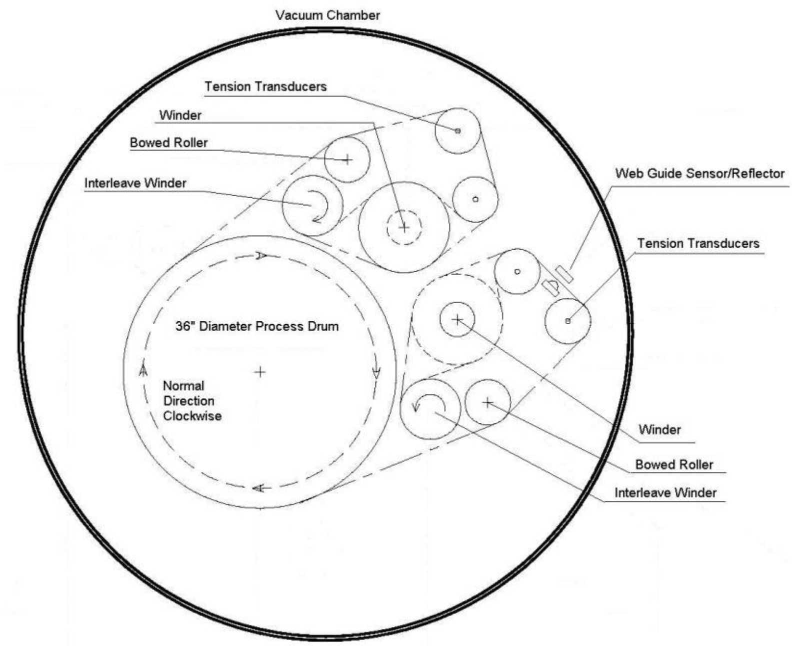

Figure 1. CHA chamber design, web can be run in forward and reverse directions

Results and Discussion:

ITO thin films were deposited with a mix of $Ar:O_2$ gas ratios and at different deposition pressures to determine ideal settings to operate the CHA tool. Films were deposited at a constant web speed, resulting in the varying film thicknesses reported in Table 1. It can be seen from Table 1 and Figure 2 that the transmission increased as the oxygen gas percentage increased. This is consistent with the band structure proposed by Hamberg and Granqvist [5], wherein oxygen vacancies and Sn^{4+} ions create shallow donor levels in the conduction band. With an increase in the number of oxygen vacancies, this donor level becomes more prominent and the result is a decrease of the band gap. These donor levels give rise to the shoulder in the transmission curves at lower oxygen percentages shown in Figure 2. The transmission values reported in Figure 2 are

Sample ID	Pressure (mTorr)	$Ar:O_2$ ratio	O2 percentage	Thickness (nm)	Average transmission in visible	Sheet Resistance (ohms/sq)
ITO-1	4	99:1	1.0	167.23	66.44	87.61
ITO-2	4	65.7:1	1.5	158.93	66.81	72.73
ITO-3	4	49:1	2.0	153.05	70.69	57.43
ITO-4	4	39:1	2.5	145.68	72.99	50.47
ITO-5	4	32.3:1	3.0	153.73	73.63	53.74
ITO-6	4	27.6:1	3.5	152.50	74.53	63.22
ITO-7	4	24:1	4.0	151.13	74.99	62.99
ITO-10	2	49:1	2.0	164.66	65.34	88.82
ITO-11	4	49:1	2.0	153.91	68.98	61.00
ITO-12	6	49:1	2.0	152.62	72.19	55.96
ITO-13	8	49:1	2.0	146.51	73.78	46.42
ITO-14	10	49:1	2.0	142.47	75.19	48.99

Table 1. As deposited properties of the ITO thin films.

of the Substrate and ITO film stack. As is typical for ITO thin films peak transmission values are seen around 550 nm with films ITO 6 and ITO 7 having values greater than 80%.

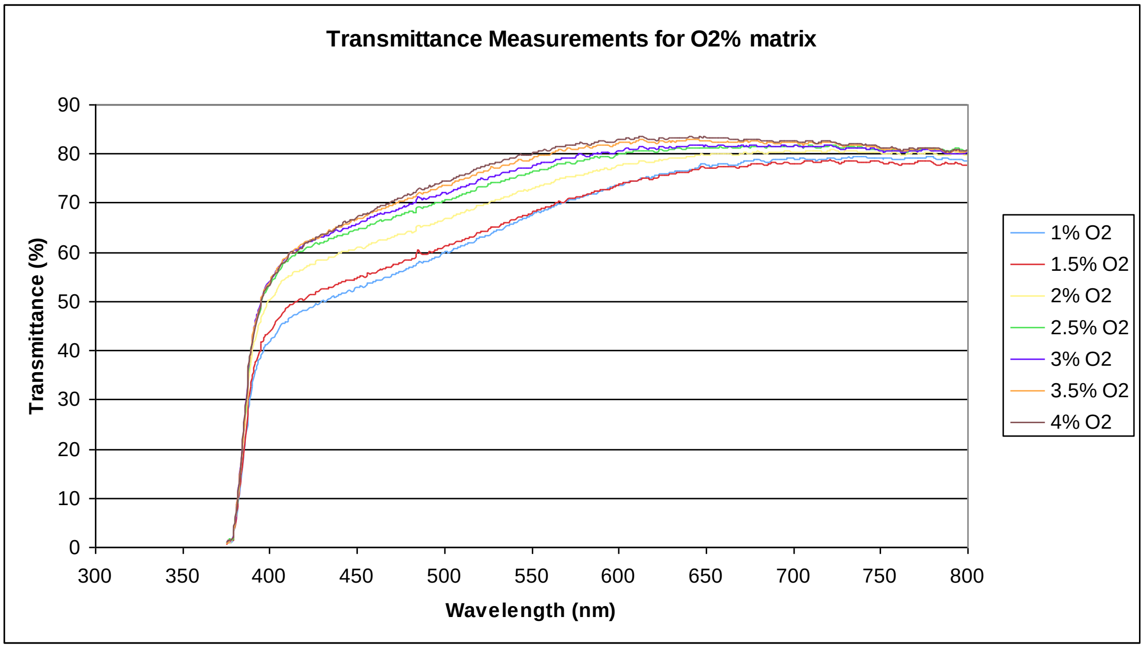

Figure 2. Transmission vs Wavelength for O_2% matrix. Transmission values are of substrate and ITO film.

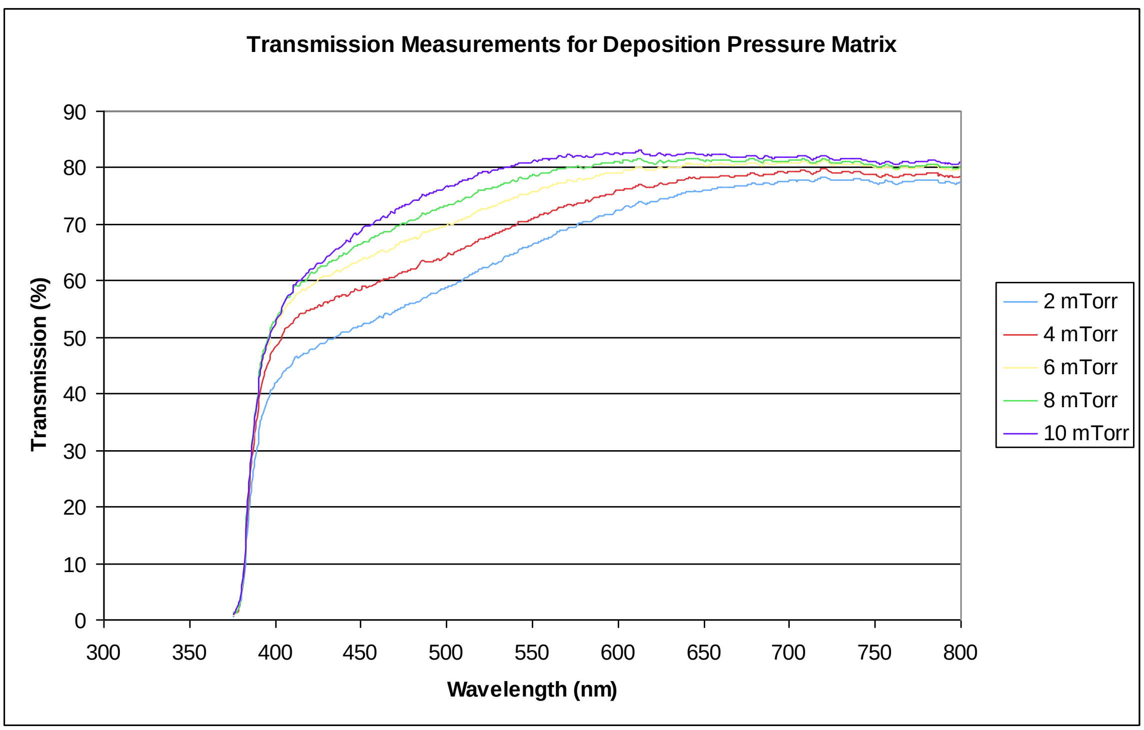

Figure 3. Transmission vs Wavelength for the deposition matrix experiment.

While O_2 % has the largest effect on the quality of deposited films it is also known that deposition pressure plays a role in final film quality. We selected 2% O_2 and investigated the effect of deposition pressure on the resultant film properties. The average transmission value for the film and substrate are included in Table 1 – samples ITO-10 – ITO-14 and is plotted in Figure 3. It can be seen that an increase in pressure leads to an increase in the transmission and a decrease in sheet resistance, with films deposited at 8 mTorr having the best overall film properties.

Post deposition annealing has been shown by many investigators to improve the quality of their films [6-14]. To investigate the effect of post deposition annealing samples were removed from the web and placed in a 110°C atmospheric oven for 30 minute increments. Table 2 is a summary of the properties following 90 minutes of annealing. Table 2 and Figures 3 show a clear trend of improvement upon post deposition annealing.

Sample ID	Pressure (mTorr)	Ar:O_2 ratio	O2 percentage	Thickness (nm)	Average transmission in visible	Sheet Resistance (ohms/sq)
ITO-1	4	99:1	1.0	167.23	67.71	71.44
ITO-2	4	65.7:1	1.5	158.93	69.54	59.31
ITO-3	4	49:1	2.0	153.05	72.78	47.50
ITO-4	4	39:1	2.5	145.68	75.52	41.61
ITO-5	4	32.3:1	3.0	153.73	76.20	42.85
ITO-6	4	27.6:1	3.5	152.50	76.92	57.17
ITO-7	4	24:1	4.0	151.13	78.46	54.17
ITO-10	2	49:1	2.0	164.66	68.08	75.39
ITO-11	4	49:1	2.0	153.91	71.83	50.89
ITO-12	6	49:1	2.0	152.62	76.04	27.47
ITO-13	8	49:1	2.0	146.51	77.10	38.46
ITO-14	10	49:1	2.0	142.47	78.02	41.16

Table 2. ITO properties following 90 minute anneal at 110° C.

	As Deposited		90 Minute Anneal	
Sample ID	Bulk Resistivity (10^-4 ohm*cm)	Figure of Merit (10^-3 ohm^-1)	Bulk Resistivity (10^-4 ohm*cm)	Figure of Merit (10^-3 ohm^-1)
ITO-1	14.65	0.23	11.95	0.37
ITO-2	11.56	0.29	9.43	0.59
ITO-3	8.79	0.74	7.27	1.28
ITO-4	7.35	1.34	6.06	2.28
ITO-5	8.26	1.44	6.59	2.50
ITO-6	9.64	1.50	8.72	2.23
ITO-7	9.52	1.71	8.19	2.96
ITO-10	14.63	0.19	12.41	0.37
ITO-11	9.39	0.53	7.83	1.00
ITO-12	8.54	1.10	4.19	4.01
ITO-13	6.80	1.95	5.63	3.61
ITO-14	6.98	2.54	5.86	4.21

Table 3. Comparison of bulk resistivity and figure of merit values for as deposited and 90 minute annealed samples. Figure of merit calculated using method proposed by Haacke in [15].

Bulk resistivity and figure of merit values were calculated for as deposited and 90 minute annealed films. The figure of merit was calculated using the equation proposed by Haacke in [15]:

$$\Phi_{TC} = T^{10}/R_s \quad \text{Equation 1}$$

Where T is the transmission at 550 nm and R_s is the sheet resistance. The bulk resistivity values for the 90 minute annealed samples show a significant improvement over the films as deposited. In all cases the figure of merit increased and for ITO-12 it increased by nearly a factor of 4. We see a similar effect when looking at the bulk resistivity values for the as deposited and annealed samples, with the decrease in the bulk resistivity of ITO-12 a factor of 2.

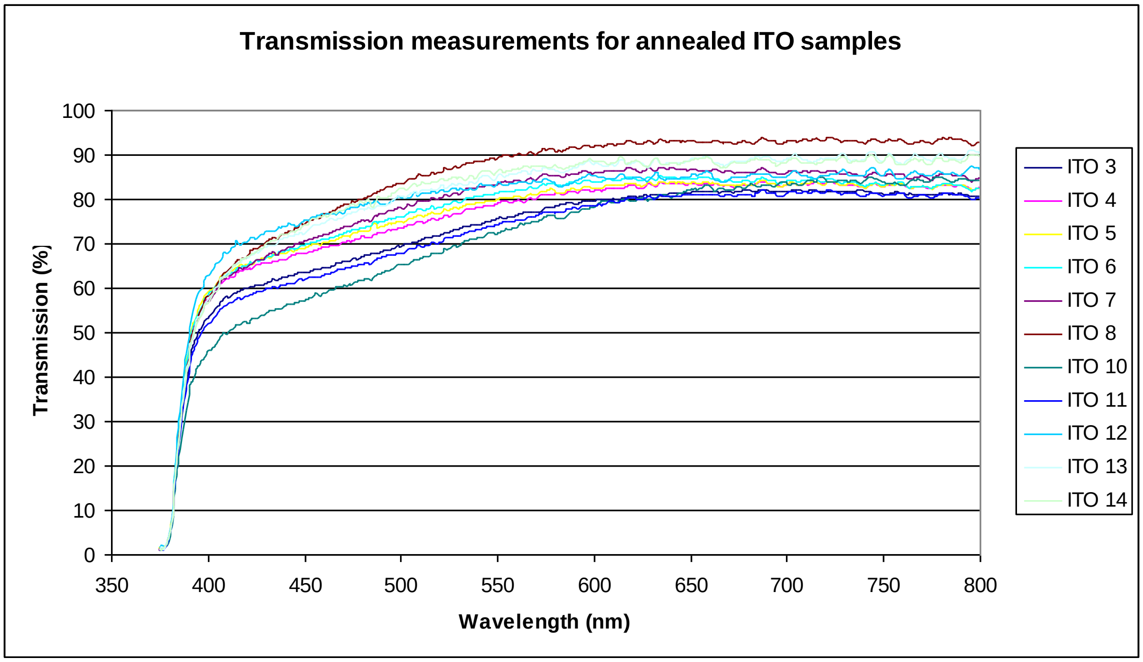

Figure 4. Transmission measurements for ITO film and substrate following after 90 minute anneal at 110° C.

Following sheet resistance and transmission measurements films were measured in a PANalytical's X'Pert Pro Materials Research Diffractometer to determine whether the films were amorphous or polycrystalline. The XRD graphs for ITO 12 as deposited and following 90 minutes of annealing are shown in Figure 4. Samples 4, 11, 12, 13 and 14 were all measured in the XRD, but due to space and clarity issues only sample 12 is shown here. A summary of relevant properties is provided in table 4 for all 5 ITO films measured in the XRD. It can be seen from Figure 4 and Table 4 that the ITO films as deposited were polycrystalline and that this crystallinity increased upon annealing. One interesting thing to note, after samples had been annealed they showed an apparent decrease in grain size for all films but ITO 13 as inferred by the diffraction peak width. These measurements correlate with previous work done by several authors that indicate the dominant scattering method in ITO films is not lattice scattering, but ionized impurity scattering [16-23]. If the dominant method of scattering were lattice scattering a decrease in the grain size as seen following annealing would likely have resulted in an increase of the sheet resistance, not a decrease as we have seen. Of note, all films show a strong preference for the [111] plane, with the ratio of the intensities of the [222]/[400] peaks remaining similar for ITO 4 and 11 and increasing for 12, 13 and 14.

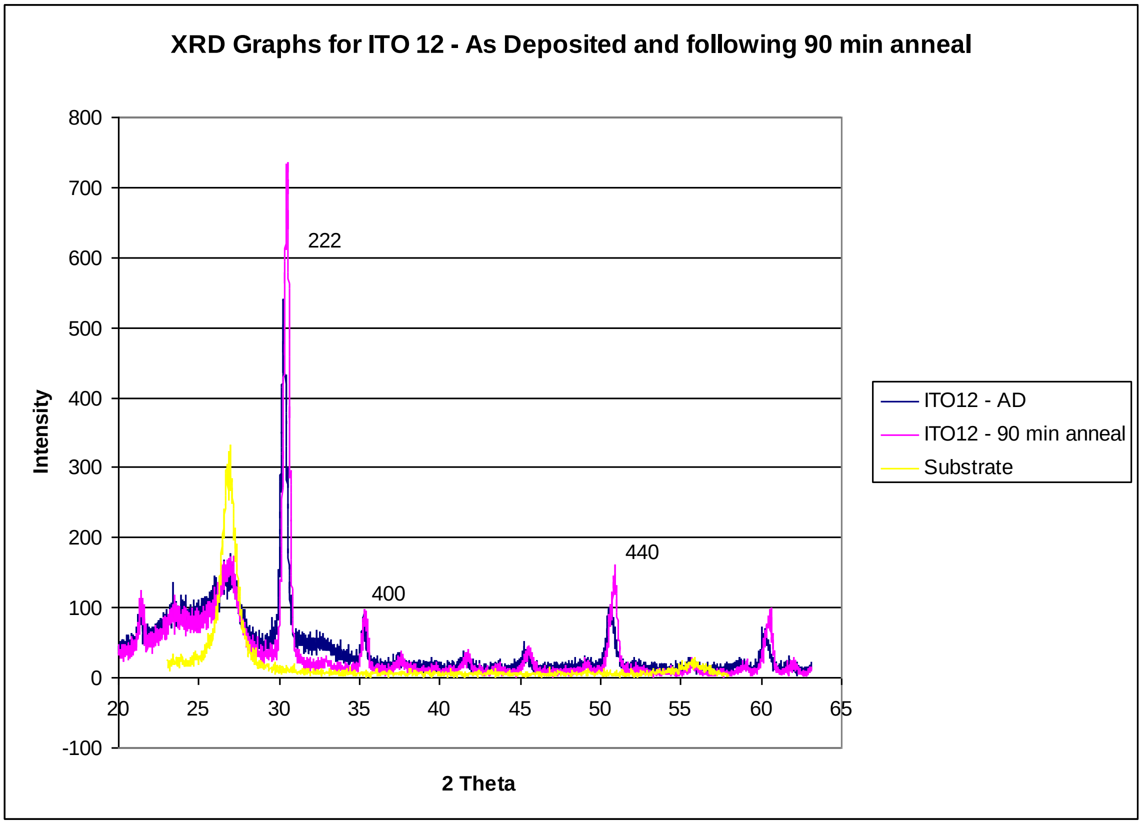

Figure 4. X-ray Diffraction measurement of the PEN substrate, ITO 12 as deposited and ITO 12 after 90 minutes of annealing.

ID	Pressure (mTorr)	O_2 %	Lattice Parameter a(Å) 0min	Lattice Parameter a(Å) 90min	Intensity Ratio (222:400) 0min	Intensity Ratio (222:400) 90min	Grain Size (Å) 0min	Grain Size (Å) 90min
4	4	2.5	10.20	10.21	8.85	8.63	545.79	218.27
11	4	2.0	10.23	10.20	6.24	5.72	722.42	311.89
12	6	2.0	10.20	10.15	8.15	9.97	722.22	397.07
13	8	2.0	10.19	10.16	9.43	12.40	240.68	256.87
14	10	2.0	10.18	10.15	10.15	16.39	541.68	363.95

Table 4. Summary of XRD data collected for samples as deposited and following 90 minute anneal times.

Conclusion:

The CAMM has deposited ITO thin films with bulk resistivity's of 6.8×10^{-4} ohm*cm with transmission values at 550 nm of 78%. After a 90 minute anneal at 110° C these values improved to 4.19×10^{-4} ohm*cm and 84%. This decrease in resistivity is believed to be due to improved crystallinity upon annealing. XRD measurements indicate deposition of polycrystalline films with a [111] preferred orientation that increases with annealing. Future work includes investigation into the etching of the ITO films, use of the ITO as a gate layer in a thin film transistor and developing a process for amorphous ITO film growth.

Sources:

1. http://www2.binghamton.edu/camm/
2. Noda K, Sato, H, Itaya H and Yamada M 2003 *Jpn. J. Appl. Phys.* **42** 217
3. Choi K, Jeong J, Kang J, Kim D, Kim J, Na S, Kim D, Kim S and Kim H 2009 *Solar Energy Mat.* **93** 1248
4. Poliks MD, Zhang H, Wickboldt P and Sammakia B 2008 *Society of Vacuum Coaters* **51** 766
5. Hamberg I and Granqvist CG 1986 *J. Appl. Phys.* **60** R 123
6. Hamdi AH, Laugal RCO, Catalan AB, Micheli AL and Schubring NW 1991 *Thin Solid Films* **198** 9
7. Frank G, Kauer E, Kostlin H and Schmitte FJ 1983 *Solar Energy Mater.* **8** 387
8. Theuwissen AJP and Declerck GJ 1984 *Thin Solid Films* **121** 109
9. Enjouji K, Murata K and Nishikawa S 1983 *Thin Solid Films* **108** 1
10. Sreenivas K, Sudersean Rao T and Mansingh A 1985 *J. Appl. Phs.* **57** 384
11. Harding GL and Window B 1990 *Solar Energy Mater.* **20** 367
12. Weijtens CHL 1991 *J. Electrochem. Soc.* **138** 3432
13. Krokoszinski HJ and Oesterlein R 1990 *Thin Solid Films* **187** 179
14. Shigesato Y, Takaki S and Haranon T 1992 *J. Appl. Phys.* **71** 3356
15. Haacke G 1976 *J. Appl. Phys.* **47** 4086
16. Clanget R 1973 *Appl. Phys.* **2** 247
17. Hoffmann H, Pickl J and Schmidt M 1978 *Appl. Phys.* **16** 239
18. Agnihotry SA, Saini KK, Saxena TK, Nagpal KC and Chandra S 1985 *J. Phys. D: Appl. Phys.* **18** 2087
19. Noguchi S and Sakata H 1981 *J. Phys. D: Appl. Phys.* **114** 1523
20. Saxen AK, Singh SOP, Thangaraj R and Agnihotri OP 1984 *Thin Solid Films* **117** 95
21. Bellingham JR, Phillips WA and Adkins CJ 1990 *J. Phs.: Condensed Matter* **2** 6207
22. Bellingham JR, Phillips WA and Adkins CJ 1991 *Thin Solid Films* **195** 23
23. Bellingham JR, Phillips WA and Adkins CJ 1992 *J. Mater. Sci. Lett.* **11** 263