JOURNAL OF MATERIALS SCIENCE 22 (1987) 1067–1080

X-ray photoelectron spectroscopic studies of sprayed CdS films

SHAILAJA KOLHE, S. K. KULKARNI*, A. S. NIGAVEKAR*, V. G. BHIDE
*School of Energy Studies and *Department of Physics, University of Poona, Pune-411007, India*

The chemical composition of sprayed CdS films has been evaluated using X-ray photoelectron spectroscopy. The general impurity content in the film is discussed, throwing light on the pyrolysis reaction involved in CdS deposition. Further, the stoichiometry of these films is studied as a function of process parameters such as pyrolysis temperature, Cd/S ratio in the solution, deposition rate and film thickness. A definite correlation is observed between composition and process parameters. The compositional variation appears to be related to the structure of CdS films as well as the growth mechanism. The effects induced by annealing in nitrogen, hydrogen and ambient air are also discussed. Hydrogen and nitrogen annealing is responsible for oxygen desorption from CdS. On the other hand air annealing induces stoichiometric variations along with oxygen intake in the films.

1. Introduction

Sprayed CdS films have applications in CdS–Cu_2S solar cells as well as in other promising cells such as CdS–$CuInSe_2$ and CdS–CdTe [1, 2]. The practical utility of spray pyrolysis lies in its technical simplicity and inexpensiveness.

The physical properties of CdS films are particularly important when Cu_2S is topotaxially deposited on CdS [3] or when CdS is used as a photoconducting element [4, 5]. The structural, electrical and optical properties of CdS films are highly sensitive to the film stoichiometry and impurity contents in the film [6, 7]. Further, since Cu_2S is generally obtained by topotaxial conversion of the top layer of CdS, the surface composition of CdS films is important. However, very few reports have appeared giving compositional details of CdS [8–14].

Here, the effects of process parameters on CdS films grown by spray pyrolysis are reported. X-ray photoelectron spectroscopy (XPS) was utilized for studying the chemical composition of sprayed CdS films. These studies were carried out with two aims in mind: to examine the stoichiometry of the films deposited under varying process parameters, and to estimate reaction by products in the films. The stoichiometry of the films depends on the process variables. The inclusion of impurities like oxygen, carbon and fragments of chemicals used in the deposition are detected. These impurities are inherent in sprayed CdS. The presence of nitrogen compounds leads to the conclusion that the pyrolysis reaction is not straightforward, but various intermediate steps are involved.

The post deposition annealing treatments in hydrogen, nitrogen and air were carried out. Hydrogen and nitrogen annealing are responsible for the reduction of oxygen content in the films. Air annealing, on the other hand, induces stoichiometric variation along with oxygen intake in the films.

2. Experimental details

The CdS films were obtained by spraying aqueous solution of cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) and thiourea [$CS(NH_2)_2$] on glass substrates maintained at 400° C [15–17]. The compressed air was used as a carrier gas for aerosol formation with a stainless steel nozzle as a spray head. The process parameters used for CdS deposition are given below:

Cd/S ratio in the solution, 1/1;
pyrolysis temperature, 400° C;
solution concentration (rate of deposition 2 μm/h), 0.1 M;
film thickness, 4 to 5 μm.

The effect of various process parameters was monitored by varying only one process parameter at a time keeping all the others the same. The ranges in which different parameters were varied are:

Cd/S ratio from 1/3 to 2/1;
pyrolysis temperature from 350 to 430° C;
solution concentration from 0.05 to 0.2 M;
film thickness from 1 to 12 μm.

All the films were analysed using XPS. Additionally, films which were annealed in H_2, N_2 and air were analysed. Annealing was carried out for 10 min in the temperature range 100 to 400° C.

XPS analysis was carried out using an ESCALAB Mark II spectrometer (VG Scientific Ltd., England). A vacuum $\sim 10^{-9}$ torr was maintained during the analysis. XPS analysis was carried out using a Mg$K\alpha$ ($h\nu$ = 1253.6 eV) source and concentric hemispherical analyser at a resolution of $\sim$0.8 eV. Au$4f_{7/2}$ level at 84.0 ± 0.1 eV was used for calibration. Argon ion gun operated at 4 kV and 20 μA was used for cleaning and profiling the CdS films.

0022–2461/87 $03.00 + .12 © 1987 Chapman and Hall Ltd.

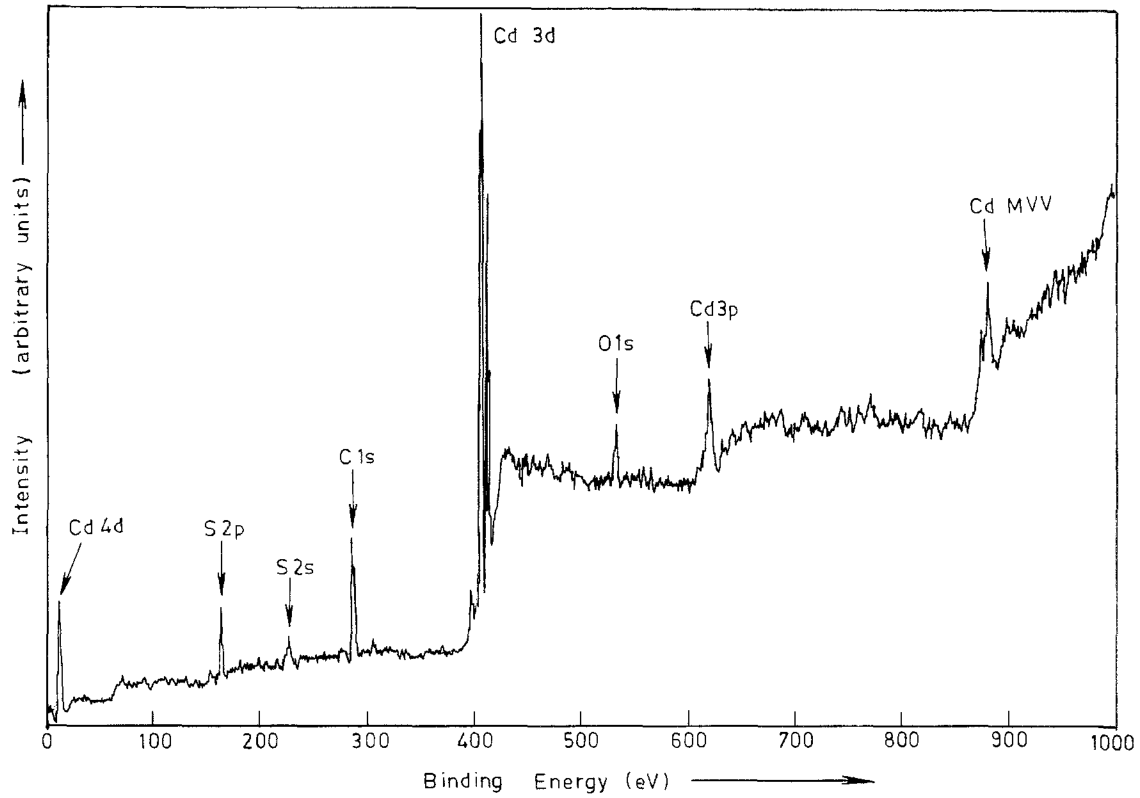

Figure 1 XPS survey scan of sprayed CdS films indicating various elements present.

3. Results and discussion

XPS investigations on sprayed CdS films indicate that composition is governed by process parameters. It is also observed that various reaction intermediates (impurities) are inherently present in spray pyrolysed CdS films. This impurity content is found in varying amounts depending on the process parameters. XPS investigations were carried out on as-received films as well as after argon ion bombardment. No appreciable change in the impurity contents was observed except after argon ion bombardment; carbon and oxygen content was reduced to small amounts. This implies that the impurities are embedded throughout the film. The stoichiometry on the surface layers of the films on ion bombardment was, however, affected due to preferential sputtering of cadmium [18, 19]. It may be noted here that the trend of Cd/S ratio variation in the film as a function of process parameters was not affected by argon ion bombardment.

We will first discuss the general impurity contents in the films and then present results regarding the stoichiometry of the films.

3.1. The nature and origin of contaminants in sprayed CdS films

The XPS survey scan of CdS film deposited under optimized conditions is depicted in Fig. 1. Impurities such as carbon and oxygen are clearly visible. Fig. 2 illustrates high resolution spectra of C 1s, O 1s, Cl 2p, Cd 3d, Cd 4d and S 2p levels.

Carbon may originate from the parent substance thiourea and/or may be incorporated during handling. The various sub-levels present are marked in Fig. 2a and are discussed in the next section. Shirreffs *et al.* [20] have shown that the water from spray solution acts as an oxygen donor in sprayed CdS films. As seen from Fig. 2a, b, both oxygen and carbon peaks are broad. Therefore the existence of more than one state cannot be ruled out. The third element present is chlorine. It is well established that chlorine is a residual part of $CdCl_2$ [7]. The variations of oxygen and chlorine contents in the film due to changes in process parameters are discussed in the next section.

As shown in Fig. 2d, Cd 3d levels are sharp. However five peaks are situated around 400.00 eV which may be attributable to nitrogen compounds [21]. The origin of these can be understood as follows. CdS films are accomplished by spraying an aqueous solution of $CdCl_2$ and CS $(NH_2)_2$. The aerosol is passed through a hot zone and then it impinges on the substrate maintained at 400° C. One end of the hot column is at 400° C while the other end (towards the nozzle) is at room temperature. While passing through the temperature gradient, various other reactions are possible. Semenov *et al.* [22] proposed two possible reactions taking place by which CdS is formed.

1. In the first reaction, a complex molecule is formed which dissociates to give CdS:

$$CdCl_2 \cdot 2(NH_2)CS \xrightarrow{3O_2} CdS \cdot 2NH_4Cl + 2CO_2 + SO_2 + N_2$$

$$CdS \cdot 2NH_4Cl \longrightarrow CdS + 2NH_4Cl \qquad (1)$$

2. In the other mechanism, hydrolysis of thiourea to urea is involved:

$$CS(NH_2)_2 \longrightarrow H_2S + H_2CN_2$$

$$H_2S + CdCl_2 \longrightarrow CdS + 2HCl$$

$$H_2CN_2 + H_2O \xrightarrow{80^\circ C} (NH_2)_2CO \qquad (2)$$

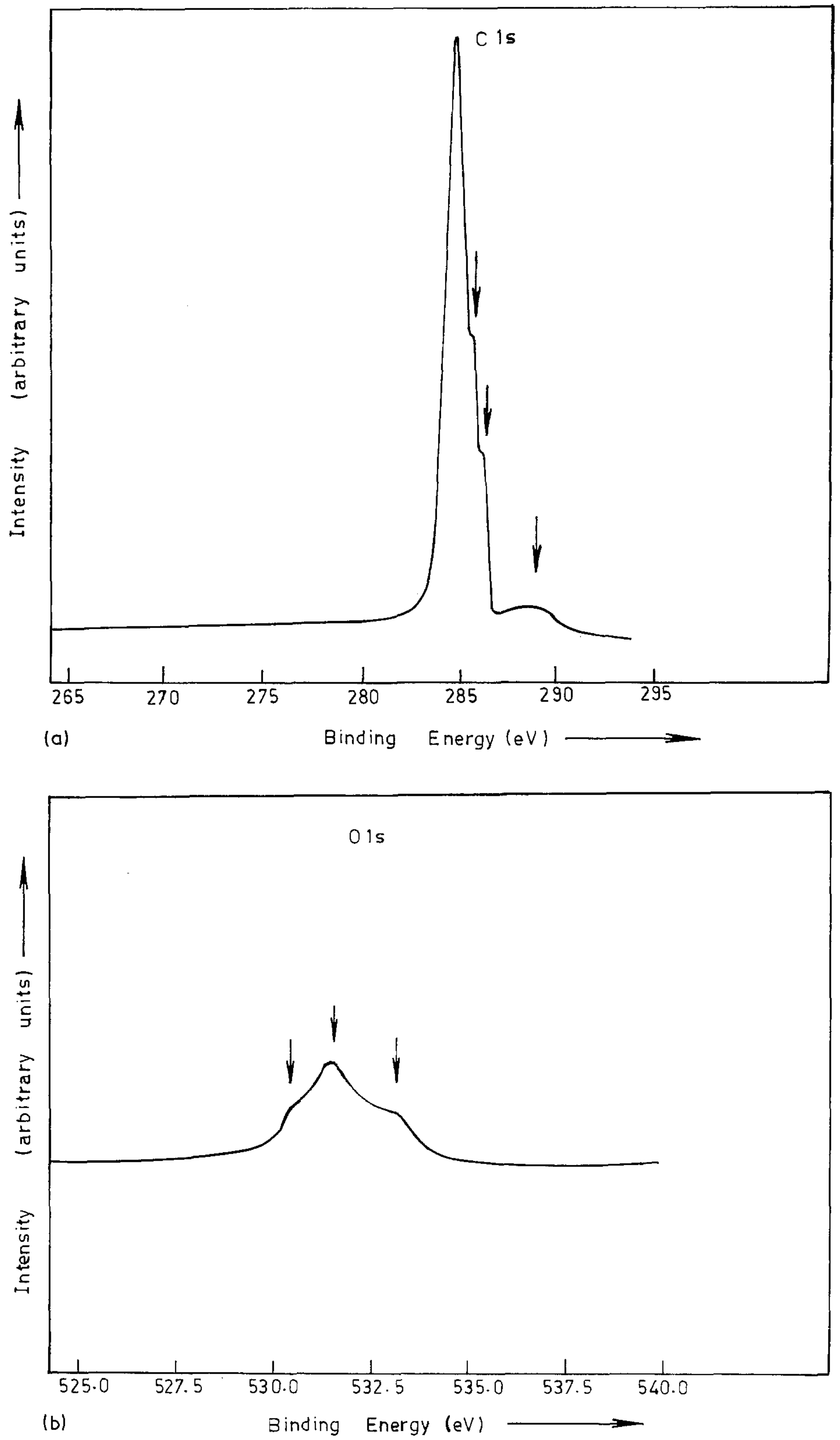

Figure 2 High resolution spectra of (a) C 1s, (b) O 1s, (c) Cl 2p, (d) Cd 3d, (e) Cd 4d and (f) S 2p levels.

The XPS peak observed at about 400.2 eV can be attributed to N 1s from $(NH_2)_2CO$ [23]. Thus reaction (2) also occurs along with reaction (1) which is quoted by various researchers [16, 24].

To analyse in more detail, XPS spectra of thiourea powder were also recorded. Fig. 3 depicts nitrogen, carbon, sulphur and oxygen regions of thiourea. N 1s level gives rise to a broad peak centred about 407.1 eV. Various other peaks can also be detected. However, the peak of interest is at 400.0 eV corresponding to urea [23]. The C 1s level of XPS of thiourea also exhibits a hump at about 288.0 eV which is attributable to urea [25]. The O 1s level is broad and more than one chemical state of adsorbed oxygen is possible. Note that the thiourea is easily converted in urea, which is confirmed by our results.

Dutault and Lahaye [26] proposed more complex compounds as intermediates. These are $CdCl_2 \cdot SCN_2H_4$, $CH_2N_2 \cdot 2HCl$, NH_4SCN, $C_9H_9N_{11}$–$HSCN$, $C_6H_9N_{11}$, $C_6H_6N_{10}$, $C_6H_3N_9$ etc. These complexes may give methyl compounds. Hence other peaks may be attributed to $(CH_3)_3N$ (N 1s at 395.2 eV) [27]; $(CH_3)_2NH$ (N 1s at 396.4 eV) [27]; $(CH_3)_3NO$ (N 1s at 402.2 eV) [23] and $C_6H_5NO_2$ (N 1s at 404.8 eV)

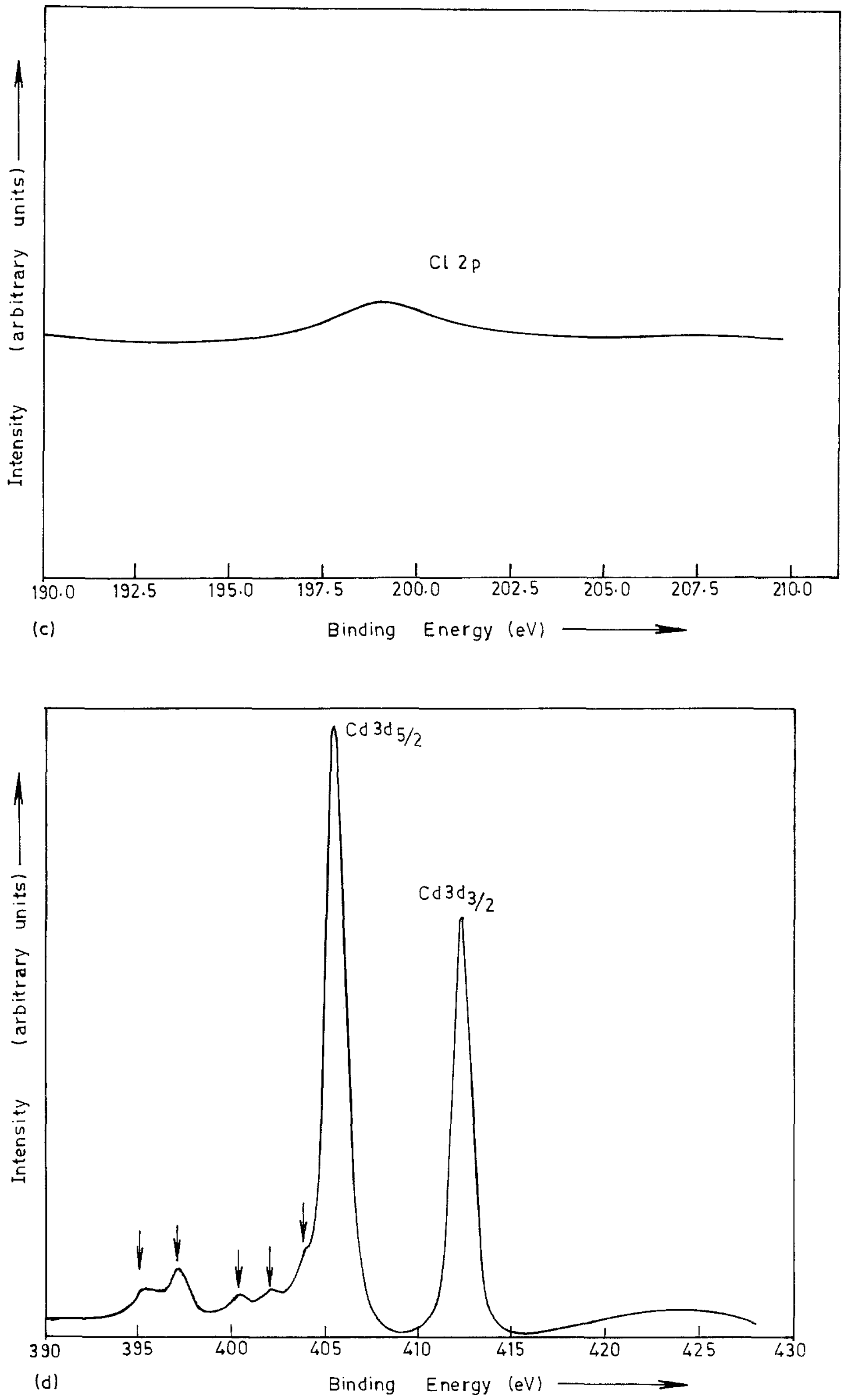

Figure 2 Continued.

[27]. However, the possibility of satellite peaks due to $MgK\alpha_3$ and $MgK\alpha_4$ at 396.6 eV and 395.0 eV also exists [23]. In Table I, the observed binding energies and possible chemical compounds are listed. The urea content in the film is found to vary with pyrolysis temperature. At lower pyrolysis temperature, incorporation of urea is favoured (see Fig. 4).

These reaction by products could not be eliminated from the films. The effects of these compounds on physical properties, however, are not known.

3.2. Dependence of process parameters on film stoichiometry

3.2.1. Cd/S ratio in the solution

The effect of Cd/S ratio in the solution on spray pyrolysed CdS films are twofold: the changes in Cd/S ratio in the solution appear to affect the growth kinetics which leads to drastic changes in the structural properties [16, 24, 32–35]. Another effect is the variation in stoichiometry.

The effect of solution composition on Cd/S ratio in

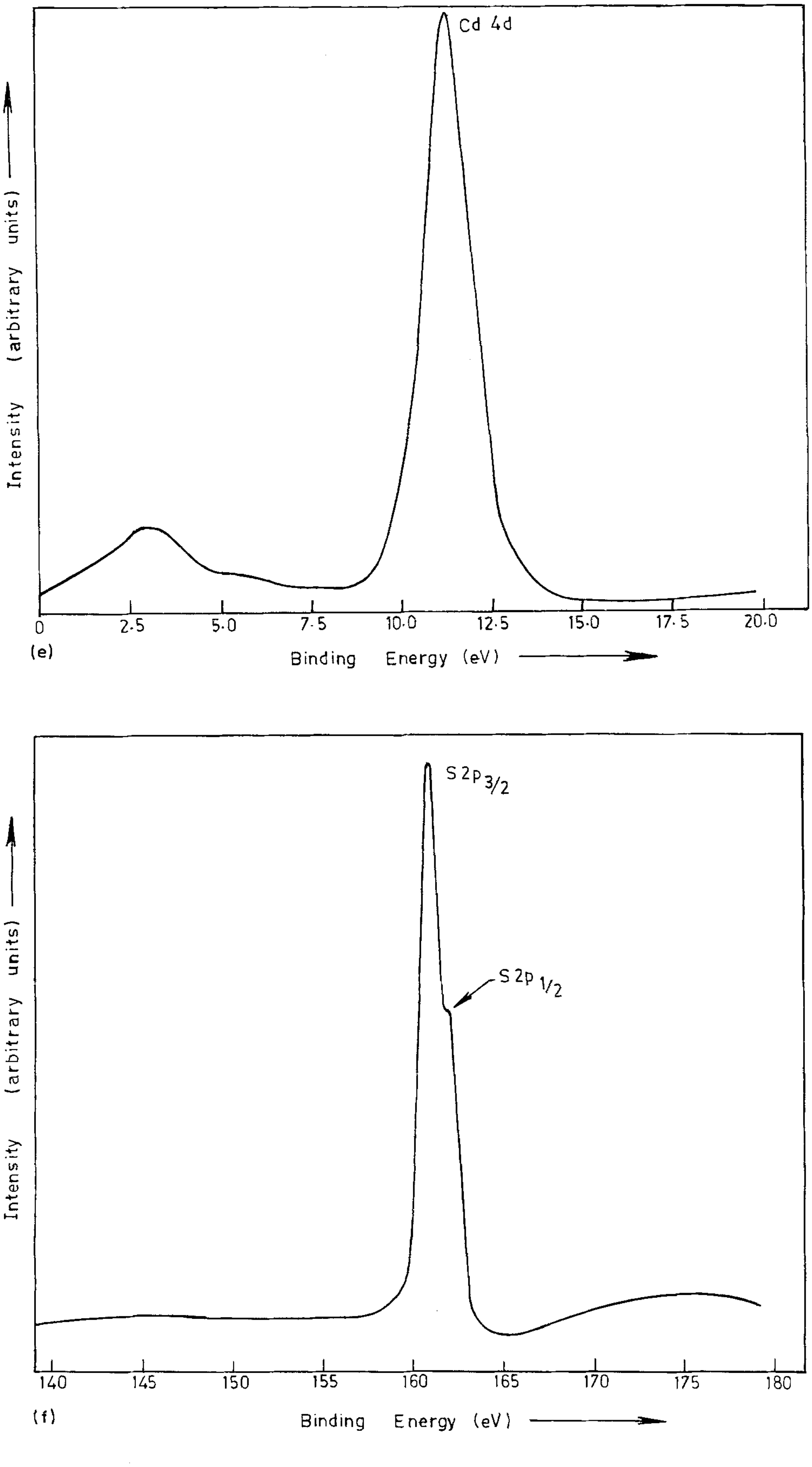

Figure 2 Continued.

the film was studied using XRF [33] and XPS [20]. There is considerable disagreement in the Cd/S ratio determined by the two methods even for 1/1 ratio in the solution.

We have attempted to estimate the stoichiometry of CdS films by measuring peak heights of Cd $3d_{5/2}$ and S 2p levels. The sensitivity factors used are those published by Briggs *et al.* [36]. Fig 5 depicts the variation of Cd/S ratio in the film as determined by XPS peak heights. The introduction of Cd ions in the solution appears to increase cadmium content in the film at a lower Cd/S ratio. However, above a certain value (Cd/S = 1.5) excess cadmium cannot be introduced in the film and hence the Cd/S ratio in the film saturates. This may be regarded as solubility limit of excess cadmium in CdS.

However, no appreciable changes in either binding energies or peak shapes of Cd 3d and S 2p levels occur.

TABLE I Observed binding energies of various elemental levels in sprayed CdS films

Energy level	Observed binding energy (eV)	Probable compound	Reported binding energy (eV)	Reference
N1s	395.2	$(CH_3)_3N$	395.8	[27]
N1s	396.4	$(CH_3)_2NH$	396.0	[27]
N1s	400.2	$(NH_2)_2CO$	400.0	[27]
N1s	402.2	$(CH_3)_3NO$	402.2	[23]
N1s	404.8	$C_6H_5NO_2$	405.1	[23]
$Cd3d_{5/2}$	405.3	CdS	405.0	[28]
$Cd3d_{3/2}$	411.4	CdS	411.7	[28]
Cd4d	11.2	CdS	11.0	[28]
$S2p_{3/2}$	161.0	CdS	161.3	[28]
$S2p_{1/2}$	162.1	CdS	162.0	[9]
C1s	285.0	$(CH_3)_2NH$ & incorporated C	285.0	[23]
C1s	285.6	$CH_3CH_2NH_2$	285.7	[25, 29]
C1s	286.3	$C_6H_5NO_2$	286.3	[21]
C1s	288.1	$(NH_2)_2CO$	288.5	[25]
C1s	530.3	Incorporated oxygen	530.0	[30]
O1s	531.4	CdO	531.3	[31]
O1s	533.9	Adsorbed water vapour	534.6	[31]
Cl2p	198.9	Chlorine in chloride form	199.1	[23]

Binding energies of cadmium and sulphur levels are listed in Table II. No conclusion can be drawn regarding the existence of other states of cadmium than Cd^{2+}. Even large changes in Cd/S ratio in the solution do not affect drastically the Cd/S ratio in the deposited films. However as we have reported earlier large variations do occur in crystalline phase and orientation [34].

3.2.2. Pyrolysis temperature

In general, increase in pyrolysis temperature is responsible for improvement in structural quality of sprayed CdS films [16]. The impurity contents in the film are also lower when pyrolysis temperature is higher [7, 16] as discussed in section 3.1.

Our XPS results also indicate that the amount of oxygen (Fig. 6a, b) and chlorine incorporated in sprayed CdS films is rather lower in films deposited at high pyrolysis temperatures. Variation of chlorine content in the film as a function of pyrolysis temperature is shown in Fig. 6b. The graph shows a decrease in chlorine content with increasing pyrolysis temperature in agreement with results previously reported [28]. The ratio of Cd $3d_{5/2}$ and O 1s peak heights is shown in Fig. 6a. The data suggest that the impurities in the film are incorporated while depositing the films. Such intake of impurities may be assisted by a large number of faults present in CdS films deposited at lower temperature [37].

A further effect of pyrolysis temperature is that the films deposited at lower pyrolysis temperature are far away from stoichiometric composition. Increase in pyrolysis temperature tends to improve the film stoichiometry. The Cd $3d_{5/2}$ to S 2p peak height ratios for films deposited at varying pyrolysis temperature are plotted in Fig. 6a. It appears that at higher pyrolysis temperature, excess Cd is evaporated, and an increment in full width at half maximum (FWHM) of Cd 4d level is also observed for films deposited at lower pyrolysis temperature (Table III).

The increment in FWHM of Cd 4d level may be associated with the higher impurity contents in the films. Note that these results indicate average composition and no distinction can be made in grain and grain boundary composition.

3.2.3. Rate of deposition

The increase in rate of deposition is achieved by increasing solution concentration. It is known that increase in the rate of deposition creates a large number of faults in the film [15]. Our results agree with this observation [37]. Along with this, it was found that stoichiometry of the films is also a function of the deposition rate. The variation in ratio of Cd $3d_{5/2}$ and S 2p peak heights for various rates of deposition are plotted in Fig. 7. Another interesting result is the increase in oxygen content in the film with decrease in deposition rate (Fig. 7). These variations in chemical composition are not associated with changes in binding energies (Table IV). From these results and changes

TABLE II XPS binding energies of various elements in sprayed CdS films deposited by varying Cd/S ratio in the solution

Cd/S in solution	Binding energy (eV)			
	Cd $3d_{5/2}$	Cd $3d_{3/2}$	S 2p	Cd 4d
1/3	405.2	411.4	160.9	10.9
1/2	405.4	411.3	160.9	11.1
1/1.5	405.0	411.6	161.2	11.3
1/1	405.3	411.5	161.0	10.7
1/0.75	405.4	411.5	161.3	10.9
1/0.5	405.1	411.3	160.8	11.0

TABLE III XPS binding energies of elements present in CdS films deposited at various temperatures

Pyrolysis temperature (° C)	Binding energy (eV)				FWHM of Cd 4d level (eV)
	Cd $3d_{5/2}$	Cd $3d_{3/2}$	S 2p	Cd 4d	
350	405.0	411.3	161.2	10.9	1.7
380	404.9	411.5	161.1	10.8	1.7
400	405.2	411.5	160.0	11.2	1.6
410	405.2	411.5	161.1	11.1	1.5
420	405.2	411.5	161.0	11.2	1.5
430	405.1	411.3	160.9	11.0	1.5

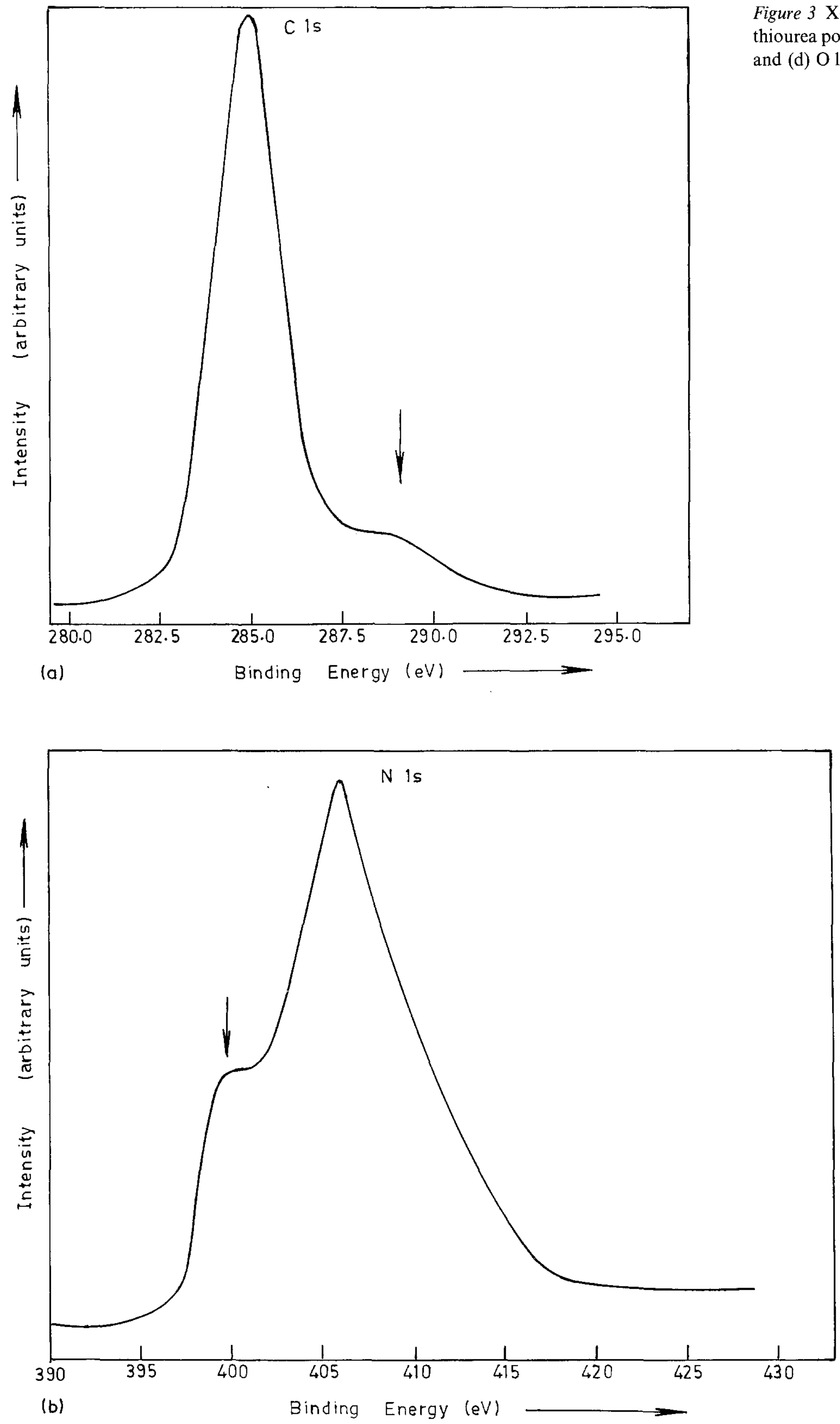

Figure 3 X-ray photoelectron spectra of thiourea powder: (a) C 1s, (b) N 1s, (c) S 2p and (d) O 1s levels.

TABLE IV XPS binding energies of various elemental levels of sprayed CdS films deposited by varying deposition rate

Solution molarity	Binding energy (eV)				FWHM of Cd 4d level (eV)
	Cd $3d_{5/2}$	Cd $3d_{3/2}$	S 2p	Cd 4d	
0.050	405.1	411.3	161.3	11.0	1.6
0.075	405.2	411.3	161.0	11.0	1.6
0.100	405.3	411.5	161.0	11.2	1.6
0.200	405.3	411.4	161.1	10.9	1.6

occurring due to pyrolysis temperature the following conclusions can be drawn.

The deposition of CdS by spray pyrolysis must be an equilibrium reaction in which Cd and S are re-evaporated and get deposited [16]. The lower deposition rate leads to rearrangement of cadmium and sulphur so that excess cadmium may be evaporated. On the other hand, when deposition rate is high, re-evaporation of cadmium may be suppressed. At

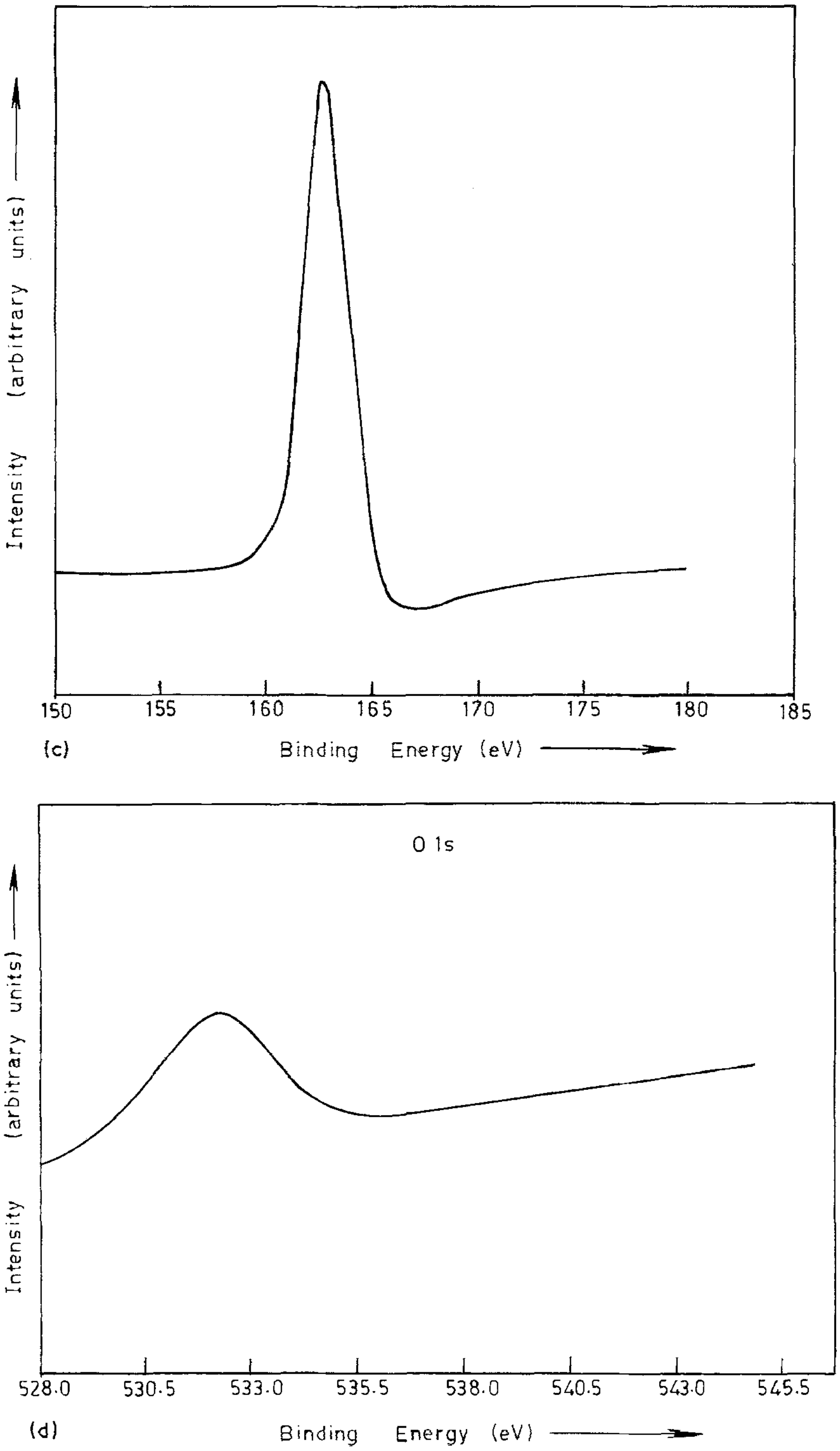

Figure 3 Continued.

high pyrolysis temperature, mobility of atoms on the substrate is higher and hence excess cadmium as well as other species may re-evaporate to give nearly stoichiometric films.

3.2.4. Film thickness

It is well established that the thin films are more susceptible to intake of impurities [38]. Our results are in agreement with this empirical rule. The oxygen content in thin films is very high (Fig. 8). However, no variation in Cd/S ratio has been detected.

3.3. Annealing induced effects in CdS films

3.3.1. Hydrogen annealing

The sprayed CdS films are known to be sensitive to oxygen capture [3]. Annealing of sprayed CdS films in non-oxidizing atmospheres is responsible for a dramatic increase in mobility and carrier concentration [2, 5, 34, 39]. The increase of mobility of films is attributable to one or more of the following [40]:

1. oxygen desorption;
2. loss of sulphur from films;
3. partial grain growth;
4. grain boundary passivation of unsaturated bonds.

Although the desorption of oxygen due to annealing in N_2 and H_2 is well established [34, 39], others are not conclusively proved. The sensitivity of XPS being higher, it was expected that minute changes in composition will be visualized.

Annealing in hydrogen resulted in a drastic decrease

TABLE V Cd/S and Cd/O ratios of films annealed in various ambients along with elemental binding energies

Condition	$\frac{H(Cd\,3d_{5/2})}{H(S\,2p)}$	$\frac{H(Cd\,3d_{3/2})}{H(O\,1s)}$	Binding energy (eV)					FWHM of Cd 4d level (eV)
			Cd $3d_{5/2}$	Cd $3d_{3/2}$	S 2p	O 1s	Cd 4d	
As-deposited	0.86	1.77	405.1	411.3	161.2	530.0 531.6 533.8	10.9	1.6
Air annealed at 200° C	0.90	2.34	405.2	411.5	161.0	530.8 531.9 533.7	11.1	1.5
Air annealed at 300° C	0.90	0.86	405.1	411.2	161.3	531.0 532.5 533.8	11.0	1.7
Air annealed at 400° C	1.00	1.87	405.3	411.4	161.3	530.9 532.3 533.8	11.6	2.1
N_2 annealed at 400° C	0.89	3.00	405.0	411.1	161.2	532.0	10.9	1.6
H_2 annealed at 400° C	0.90	3.77	404.8	411.5	161.1	532.4	11.0	1.6

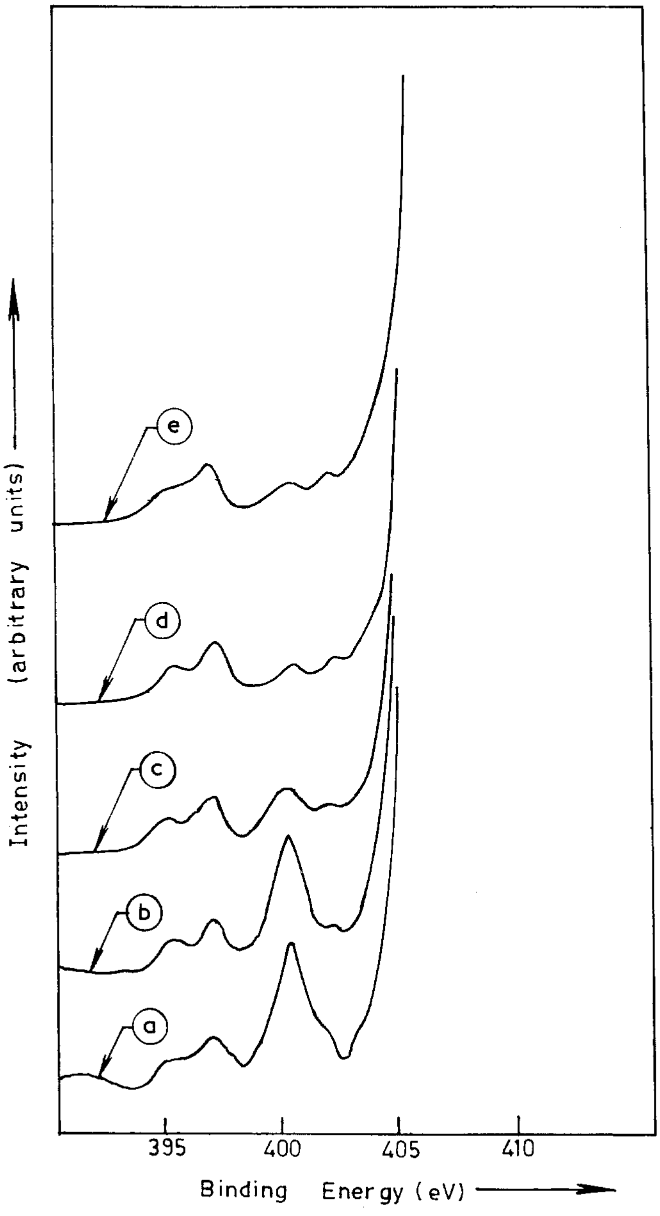

Figure 4 XPS scan of N 1s level of sprayed CdS films deposited at (a) 350, (b) 380, (c) 400, (d) 420 and (e) 430° C.

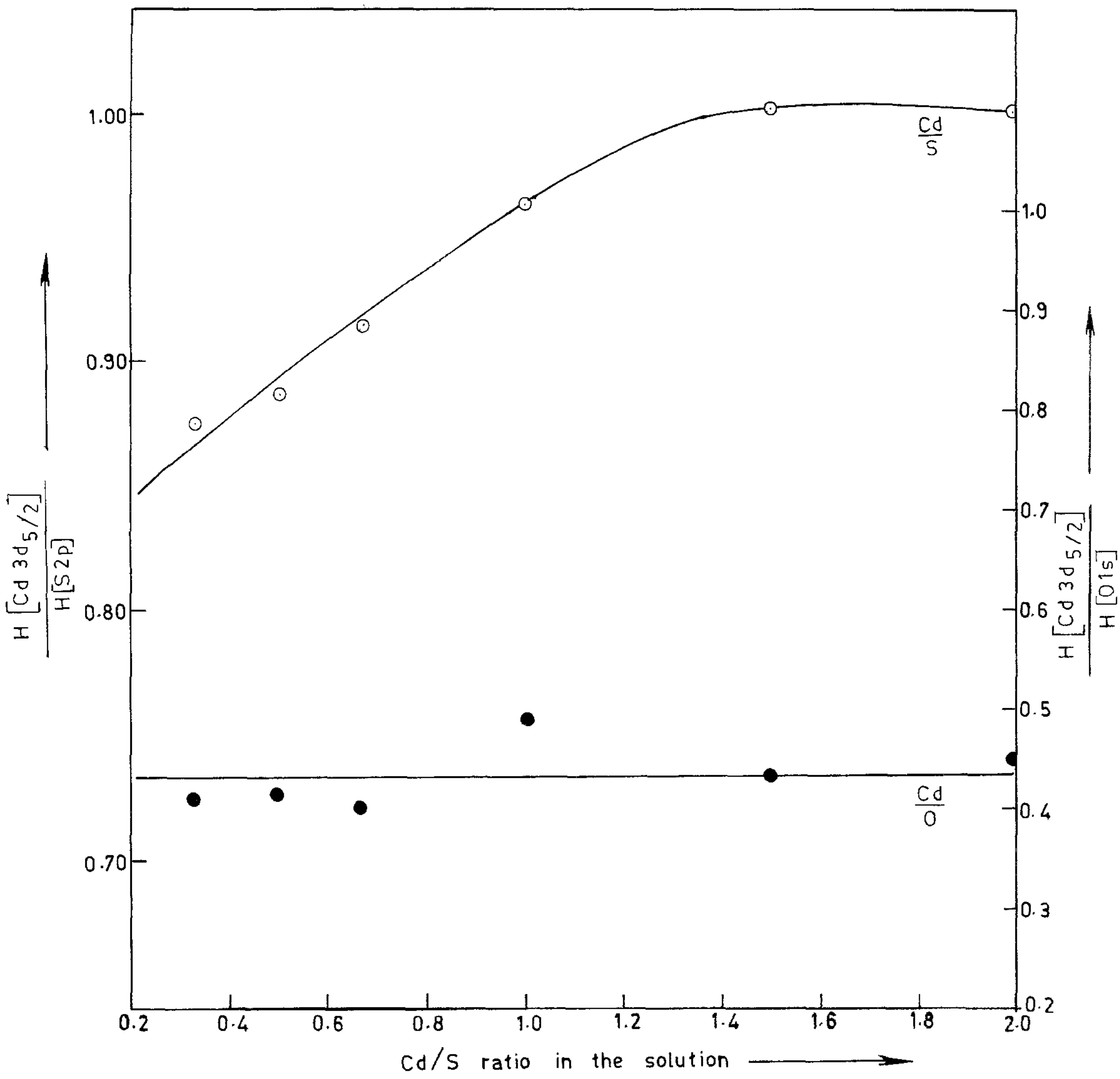

Figure 5 Cd $3d_{5/2}$/S 2p and Cd $3d_{5/2}$/O 1s peak height ratios as a function of Cd/S ratio in the spray solution.

in oxygen content (Table V). Very little change was however observed in the Cd/S ratio.

3.3.2. Nitrogen annealing

Annealing in N_2 also caused a decrease in oxygen content in the film, but the effect is less pronounced than that of H_2 annealing treatment.

3.3.3. Air annealing

The importance of air annealing lies in its effect on photo-conductivity [41, 42]. The compositional changes induced by air annealing are previously reported on single crystal [8] and chemically deposited CdS films [13], and screen printed CdS layers [12].

We observed some interesting results. Up to annealing temperatures of about 300° C, total oxygen content in the film increases (Table V) and above 300° C, oxygen appears to be desorbed from CdS films. The binding energy of the major O 1s peak is 532.5 eV which suggests the presence of oxide content in CdS [37]. However, the peak is rather broad and peaks at 530.8 eV and 533.8 eV may be present (Fig. 9). The peak at 533.8 eV may be due to adsorbed water vapour [37] while that at 530.8 eV can be attributed to Cd–O phase [38]. At an annealing temperature of 400° C, the existence of two phases of oxygen is clearly seen at 532.3 eV and 530.8 eV (Fig. 9). Although no change in binding energies of Cd 3d level and O 1s are observed, the peaks of O 1s are clearly due to adsorbed oxygen [37] and CdO [38], respectively.

The Cd/S ratio is also found to vary with annealing temperature (Table V). Air annealing causes sulphur vacancies in sprayed CdS films. The effect of this non-stoichiometry is to increase the mobility and hence the conductivity of sample [28]. We observed a decrease in resistivity due to air annealing. The details are given elsewhere [37].

4. Conclusions

In conclusion, the following points can be noted.

1. These studies reveal the fact that various impurities are incorporated in sprayed CdS films which are by-products of the pyrolysis reaction. These impurities originate from thiourea and are inherent in sprayed CdS films. The presence of these impurities supports the intermediate chemical reactions suggested by Semenov *et al.* [22] and Dutault *et al.* [26].
2. The stoichiometry of sprayed CdS films is found to depend on the actual process parameter used. Excess cadmium in the solution causes increase in cadmium content of the film up to a certain limit.

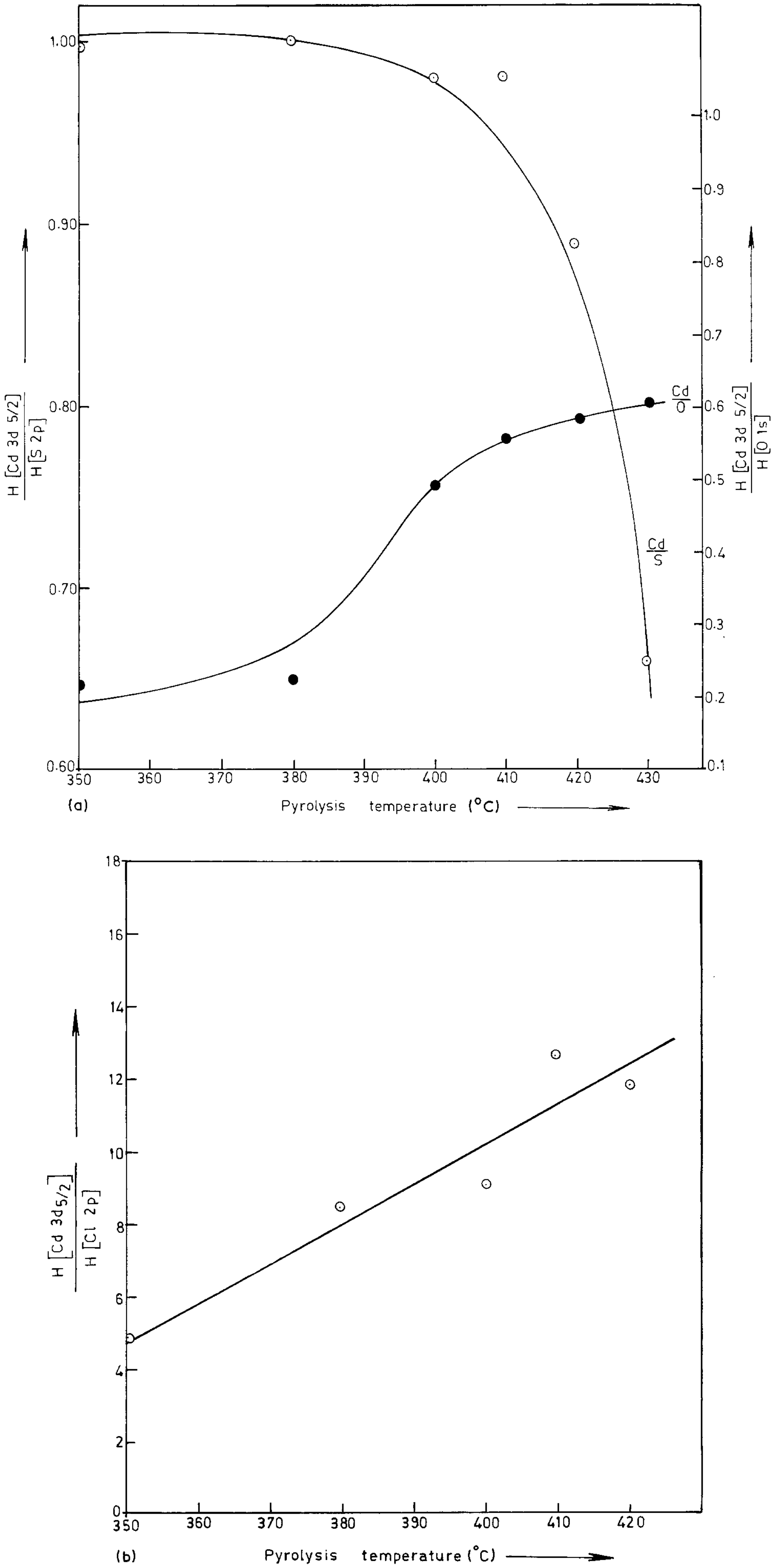

Figure 6 (a) Cd $3d_{5/2}$/S 2p and Cd $3d_{5/2}$/O 1s XPS peak height ratios for films deposited at various pyrolysis temperatures. (b) Cd $3d_{5/2}$/Cl 2p XPS peak height ratio as a function of pyrolysis temperature.

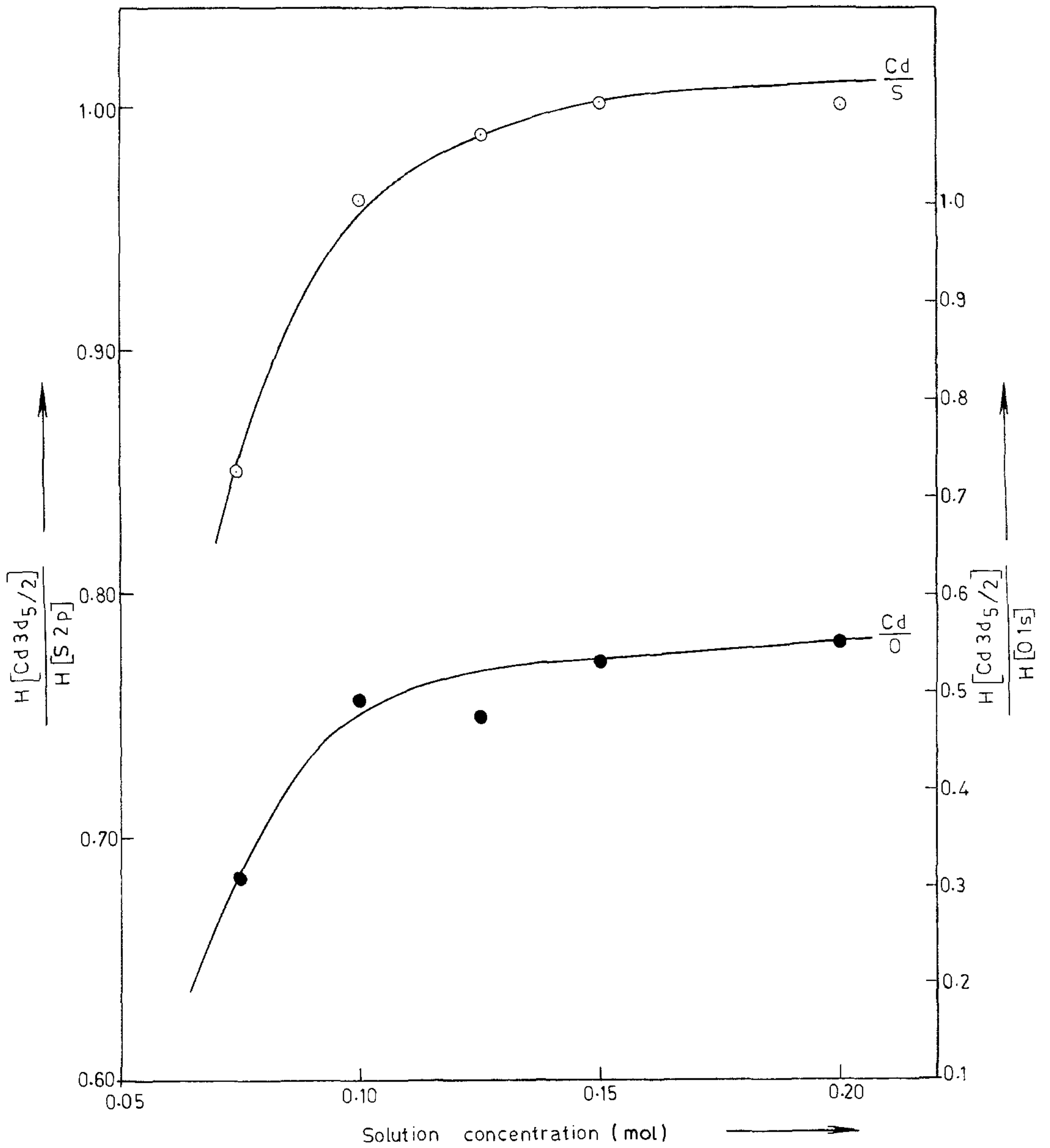

Figure 7 Cd $3d_{5/2}$/S 2p and Cd $3d_{5/2}$/O 1s XPS peak height ratios of the films deposited at varying solution concentrations.

Pyrolysis temperature and deposition rate on the other hand govern stoichiometry of the films by equilibrium between deposition and re-evaporation processes. High pyrolysis temperature and lower deposition rates lead to more stoichiometric films.

3. Hydrogen annealing leads predominantly to oxygen desorption from the films. The stoichiometric changes are, however, small.

Air annealing induces stoichiometric variations along with oxygen incorporation in the films, leading to the formation of two states of oxygen in CdS. One is the Cd–O phase while the other is chemisorbed oxygen.

Acknowledgements

The authors wish to thank Professor B. R. Marathe and Dr M. G. Takwale for the helpful discussions. Financial support from the Department of Non-Conventional Energy Sources (New Delhi) and the Department of Science and Technology (New Delhi) is acknowledged.

References

1. A. M. HERMANN, L. FABICK, K. ZWEIBEL and R. HARDY, In Proceedings of the 16th IEEE Photo. Sp. Conf. (IEEE, New York, 1982) p. 840.
2. Y. Y. MA, A. L. FAHRENBRUCH and R. H. BUBE, *Appl. Phys. Lett.* **30** (1977) 423.
3. M. SAVELLI and J. BOUGNOT, "Topics in Applied Physics" No. 31 (Springer Verlag, Berlin, 1979) p. 213.
4. D. RICHARDS, A. M. EL-KORASHY, R. J. STIRN and P. C. KARULKAR, *J. Vac. Sci. Technol.* **A2** (1984) 332.
5. J. W. ORTON, B. J. GOLDSMITH, J. A. CHAPMAN and M. J. POWELL, *J. Appl. Phys.* **53** (1982) 1602.
6. J. BOUGNOT, M. PEROTIN, J. MARUCCHI, M. SIRKIS and M. SAVELLI, in Proceedings of the 12th IEEE Photo. Sp. Conf. (IEEE, New York, 1976) p. 519.
7. F. DUTAULT and J. LAHAYE, *Rev. Phys. Appl.* **15** (1980) 579.
8. Y. YAMAGUCHI and K. NAGAI, *Jpn J. Appl. Phys.* **13** (1974) 1897.
9. L. J. BRILLSON, R. S. BAUEV, R. Z. BACHRAIH and J. C. McMENAMIN, *J. Vac. Sci. Technol.* **17** (1980) 476.
10. D. LICHTMAN, J. H. CRAIG, V. SAILER and M. DRINKWINE, *Appl. Surf. Sci.* **7** (1981) 325.

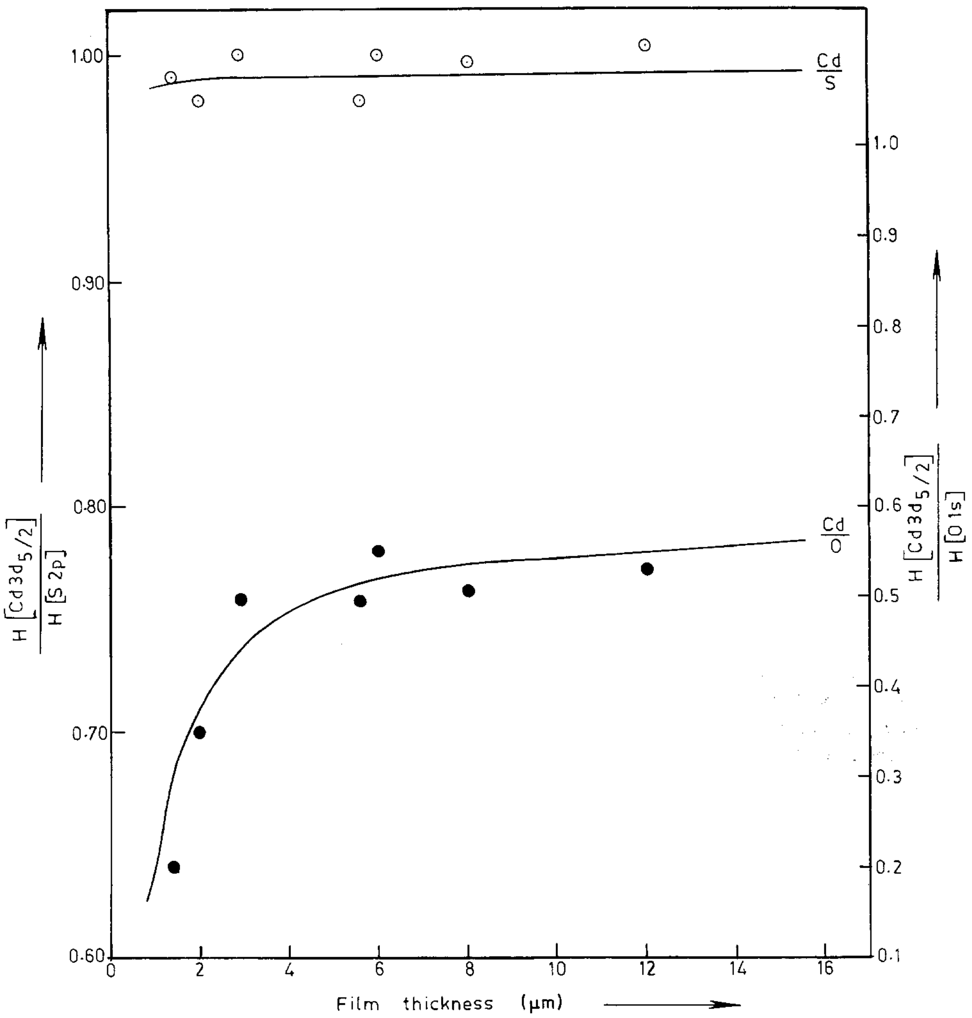

Figure 8 A plot of Cd $3d_{5/2}$/S 2p and Cd $3d_{5/2}$/O 1s peak height ratios against film thickness.

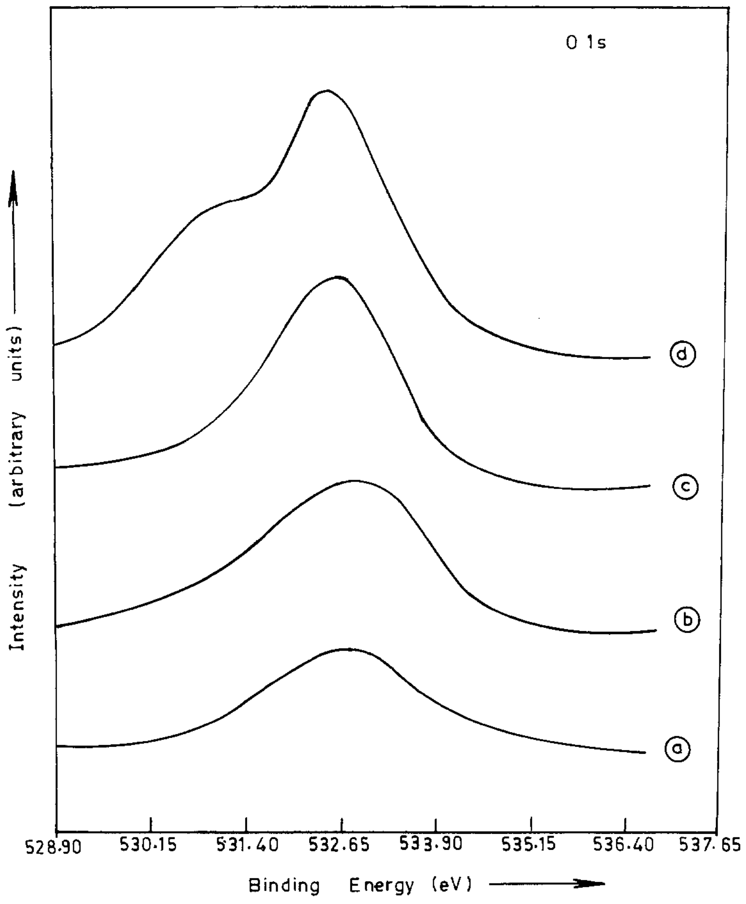

Figure 9 High resolution XPS scan of O 1s level for (a) untreated sample, and samples annealed in air at (b) 200, (c) 300 and (d) 400° C.

11. M. L. LICHTENSTEIGER and C. WEBB, *Appl. Phys. Lett.* **38** (1981) 323.
12. D. P. AMALNERKAR, S. BADRINARAYAN, S. K. DATE and A. P. B. SINHA, *Appl. Phys. Lett.* **41** (1982) 270.
13. S. KOLHE, S. K. KULKARNI, A. S. NIGAVEKAR and S. K. SHARMA, *Solar Energy Materials* **10** (1984) 47.
14. W. J. DANAHER, L. E. LYONS and G. C. MORRIS, *ibid.* **12** (1985) 137.
15. Y. Y. MA and R. H. BUBE, *J. Electrochem. Soc.* **124** (1977) 1430.
16. M. PEROTIN, Ph.D. Thesis, University of Montpellier, France, 1981.
17. J. B. MOONEY and S. B. RADDING, *Ann. Rev. Mater. Sci.* **12** (1982) 81.
18. V. H. H. ANDERSON, H. L. BAY, R. BEHRISCH, M. T. ROBINSON, H. E. ROOSENDAAL and P. SIGMUND, in "Sputtering by Particle Bombardment" Vol. I, edited by R. Behrisch (Springer Verlag, Berlin, 1981).
19. M. P. SEAH, *Thin Solid Films* **81** (1981) 879.
20. B. F. SHIRREFFS, C. H. CHENG, K. GEIB and K. A. JONES, *J. Electrochem. Soc.* **131** (1984) 440.
21. K. SIEGBAHN, C. NORDLING, A. FAHLMAN, R. NORDBERG, K. HAMRIN, S. HEDMAN, G. JOHNSON, J. BERGMARK, S. KARLSSON, I. LINDGREN and B. LINDBERG, "ESCA Atomic Molecular and Solid State Structure Studies by means of Electron Spectroscopy", (Almquist and Wisells, Boktryckerii AB, Uppasala, 1967) p. 108.
22. V. N. SEMENOV, E. M. AVERBAKH and L. A. MIKIHALEVA, *Zh. Neorg. Khim.* **24** (1979) 579.
23. T. A. CARLSON, "Photoelectron and Auger Spectroscopy" (Plenum, New York, 1976) p. 349.
24. R. R. CHAMBERLIN and J. S. SKARMAN, *J. Electrochem. Soc.* **113** (1966) 86.
25. U. GEDIUS, P. F. HEDEN, J. HEDMAN, B. S. LINDBERY, R. MANNE, R. NORDBERG, C. NORDLING and K. SEIGBAHN, *Phys. Scr.* (1970) 70.
26. F. DUTAULT and J. LAHAYE, *Bull. Soc. Chim (France)* **5–6** (1970) I-256.
27. Z. B. MAK SIC and K. RUPNIK, *Z. Naturforsch* **35** (1980) 998.
28. V. G. BHIDE, S. SALKALACHEN, A. C. RASTOGI, C. N. R. RAO and M. S. HEGDE, *J. Phys. D. Appl. Phys.* **14** (1981) 1647.
29. M. W. ROBERTS, "Advances in Catalysis" Vol. 29 (Academic Press, New York, 1980) p. 55.
30. C. J. VESELY and D. W. LANGER, *Phys. Rev.* **B4**, (1971) 451.
31. J. C. FUGGLE, "Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy", edited by D. Briggs (Heyden and Sons, London, 1977) p. 295.
32. K. L. CHOPRA and S. R. DAS, "Thin Film Solar Cells" (Plenum Press, New York, 1983) p. 298.
33. J. RECKTENWALD, J. B. MOONEY, L. MCINTOSH, R. H. LAMEREAUX, C. W. BATES Jr., ATIQ RAZA and K. NELSON, *Electrochem. Soc.* Spring Meeting (1981).
34. S. KOLHE, S. K. KULKARNI, M. G. TAKWALE and V. G. BHIDE, *Solar Energy Materials* **13** (1986) 203.
35. R. K. GUPTA and O. P. AGNIHOTRI, *Solid State Commun.* **23** (1977) 225.
36. D. BRIGGS and M. P. SEAH, "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy" (Wiley, New York, 1983) p. 511.
37. S. KOLHE, S. K. KULKARNI, M. G. TAKWALE, B. R. MARATHE and V. G. BHIDE, *Solar Energy Materials* (in press).
38. L. I. MAISSEL and R. GLANG, "Handbook of Thin Film Technology" (McGraw-Hill, New York, 1970) p. 85.
39. F. B. MICHLETTI and P. MARK, *Appl. Phys. Lett.* **10**, (1967) 136.
40. R. H. BUBE and A. L. FAHRENBRUCH, "Fundamentals of Solar Cells" (Academic Press, New York, 1983) p. 381.
41. R. H. BUBE, "Photoconductivity in Solids", (Wiley, New York, 1960) p. 175.
42. A. A. URITSKAYA, V. P. PANOV, N. D. BETENEKOV, I. I. POLEZHAEV, G. D. SIZOVA and G. A. KITAEV, *Neorganicheskie Mater.* **12** (1976) 193.

Received 6 May
and accepted 23 July 1986