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Composition, surface morphology and structure of *n*-CdSe films prepared by repeated cycles of electrodeposition

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A modified selective electrodeposition technique employing three cycles of deposition, annealing and *in situ* etching has been used to grow *n*-CdSe films. The results of our investigations on the composition, surface morphology and structure of the films are also discussed. In comparison to the CdSe films obtained by a single cycle of electrodeposition, it is shown that the repeated cycle of deposition yields a more regular and less porous film with larger grain sizes.

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1. Introduction

Cathodic electrodeposition of compound semiconductors has been investigated by a large number of workers [1–12]. A unique feature of electrodeposition is that it can yield relatively pure films from less pure solutes. This can be accomplished either by an electrolytic purification step before deposition, or using a suitable complexant in the electrolyte to suppress the impurities (selective electrodeposition). Recently we have fabricated CdSe films by a selective electrodeposition process using ethylene diamine tetra-acetic acid (EDTA) as a complexant [13, 14]. The photoelectrochemical solar cells fabricated from these films yielded open circuit voltage, 470 mV; short circuit current, 8 mA cm^{-2}; efficiency, 3.6%; and fill factor, 0.38. In an endeavour to improve the performance of the selectively electrodeposited films, a detailed analysis of solid-state properties was carried out. A correlation between the physical properties and observed cell performance was also established. Our studies indicated that the electrodeposited CdSe films are usually porous. Further attempts were therefore made to modify the electrodeposition process so that the film porosity may be reduced, and larger grain sizes are also obtained. The results of our investigations on the composition, surface morphology and structure of the CdSe films fabricated by the unmodified and the modified selective electrodeposition technique are reported.

2. Experimental procedure

2.1. Sample preparation

Cadmium selenide films were electroplated at 49 °C in an aqueous electrolyte containing AR grade 0.3 M $CdSO_4$, 0.9×10^{-3} M SeO_2 and 1.5×10^{-2} M ethylene diamine tetraacetic acid. The cathodic electrodeposition was carried out under potentiostatic conditions on a nickel substrate at − 0.68 V against a saturated calomel electrode (SCE). A platinum plate was used as the anode. Prior to electrodeposition, the nickel plates were first polished by a 600 grit emery paper and then thoroughly cleaned [14].

Two sets of CdSe films were prepared. In set I (film A) a single cycle of electrodeposition for 10 min was used. The freshly prepared films were annealed in air at 400 °C in slow steps. In set II (film B) the CdSe films were prepared by employing three cycles of deposition, *in situ* etching and annealing steps. In the first cycle, the CdSe films were electroplated for 3.5 min and then annealed in air at 340 °C. The annealed CdSe films were washed thoroughly with triple distilled water. The freshly washed and dried films were again used as cathodes for the second cycle of electrodeposition. Before beginning the second cycle, the CdSe films were etched *in situ* in the electrodeposition bath by applying a small anodic bias to the working electrode. The etching current density was controlled by an external load; etching current density and etch duration were also optimized by studying the photoanodic behaviour of the electrodeposited films. An etching current density of 0.14 mA cm^{-2} for 60 s was found to be optimum, and was used in the present work. Immediately after the *in situ* etching, a cathodic polarization of − 0.68 V was impressed on the cathode and electrodeposition was carried out for 3.5 min. The CdSe films prepared after the second cycle were again subjected to similar annealing steps, followed by *in situ* etching. A third cycle of electrodeposition at − 0.68 V for 3 min was again employed. The final

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annealing after the third cycle of electrodeposition was carried out at 400 °C in air.

2.2. Compositional analysis

Auger depth profiles of the CdSe films before and after annealing at 240 and 340 °C were obtained under ultra-high vacuum conditions in a set-up supplied by VG scientific, UK. Auger spectra were obtained using a normal incidence electron gun and a cylindrical mirror analyser. An argon ion gun was operated at 3 kV with a current of 10 μA to sputter-etch the samples in a controlled manner. The Auger transitions between 50 and 1000 eV were sequentially scanned after each sputter cycle. The modulation used was 2 V peak-to-peak for peaks below 120 eV, and 4 V peak-to-peak above it. The film composition was determined by measuring peak-to-peak heights of Auger peaks corresponding to Cd MNN, Fe LMM, Zn LMM, Cu LMM, Pb NOO, Se MNN, S LMM, O KLL and Cl LMM, and the data were analysed using a method described by Palmberg *et al.* [15].

2.3. SEM studies

Scanning electron microscopy was carried out with a Jeol JSM 35CF scanning electron microscope at 20 kV using normal incidence.

2.4. Structural analysis

The X-ray diffraction data of the CdSe films were recorded on a Philips Automated Powder X-ray diffractometer model PW-1700 using Cu*K*α radiation.

3. Results and discussions

3.1. Single-cycle electrodeposition

The plating characteristics of CdSe on bare nickel and CdSe-coated annealed Ni cathodes are shown in Fig. 1. Both characteristics are typical of a diffusion-limited electrodeposition process [16]. A small shift of 40 mV in the onset potential for selenium deposition on the CdSe-coated nickel cathode was observed. However, the cadmium onset remained unchanged. The plateau regions denoting the limiting current deposition are also confined within the same potential range for the two cases. These results indicate that the overpotential for CdSe deposition can be regarded as practically similar for the two cases.

Cathodic electrodeposition from an aqueous acidic bath normally yields CdSe films inherently rich in selenium. This is because of the following reactions which occur at the cathode during the electrodeposition:

$$H_2SeO_3 + 6H^+ + 6e \rightarrow H_2Se + 3H_2O \quad (1)$$

$$Cd^2 + H_2Se \rightarrow CdSe + 2H^+ \quad (2)$$

$$2H_2Se + H_2SeO_3 \rightarrow 3Se + 3H_2O \quad (3)$$

Reaction 2 leads to the deposition of CdSe while reaction 3 causes the deposition of elemental selenium at the cathode. The inherent excess of selenium in CdSe films is due to the strong competition of reaction 3 with reaction 2 [17]. The insulating nature of the selenium tends to make the cathode surface become passive as the electrodeposition is continued for a longer duration. The subsequent CdSe layers thus become porous.

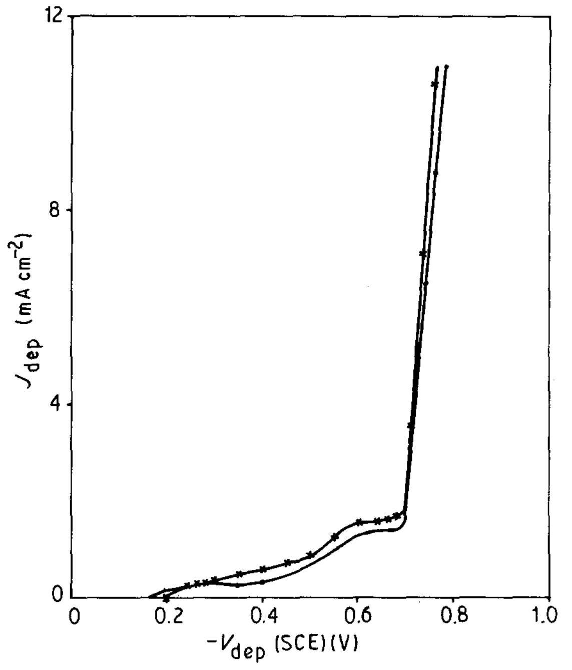

Figure 1 Cathodic polarization characteristics for (●) bare nickel cathode and (×) CdSe coated nickel cathode.

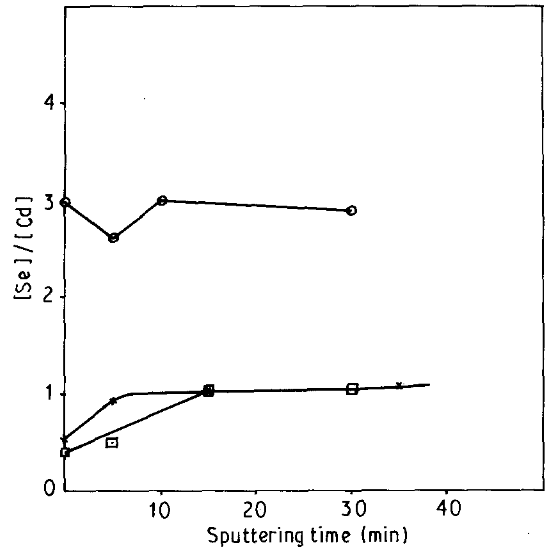

Figure 2 Variation of the Se/Cd ratio with sputtering time for CdSe films: (○) unannealed, annealed at (×) 240 °C and (□) 340 °C.

Auger electron spectra of the CdSe films indicated the presence of peaks corresponding to Cd (M N N), Se (M N N), O (K L L) and Cl (L M M) in the annealed films. However, no oxygen was detected in the unannealed films. The variation of Se:Cd ratio with sputtering time for unannealed, 240 and 340 °C annealed CdSe films are shown in Fig. 2. The bulk Se:Cd ratio for the unannealed films was found to be high, as was expected from reaction 3. The excess selenium was, however, removed on annealing. The surface-layer stoichiometry of the CdSe films annealed at

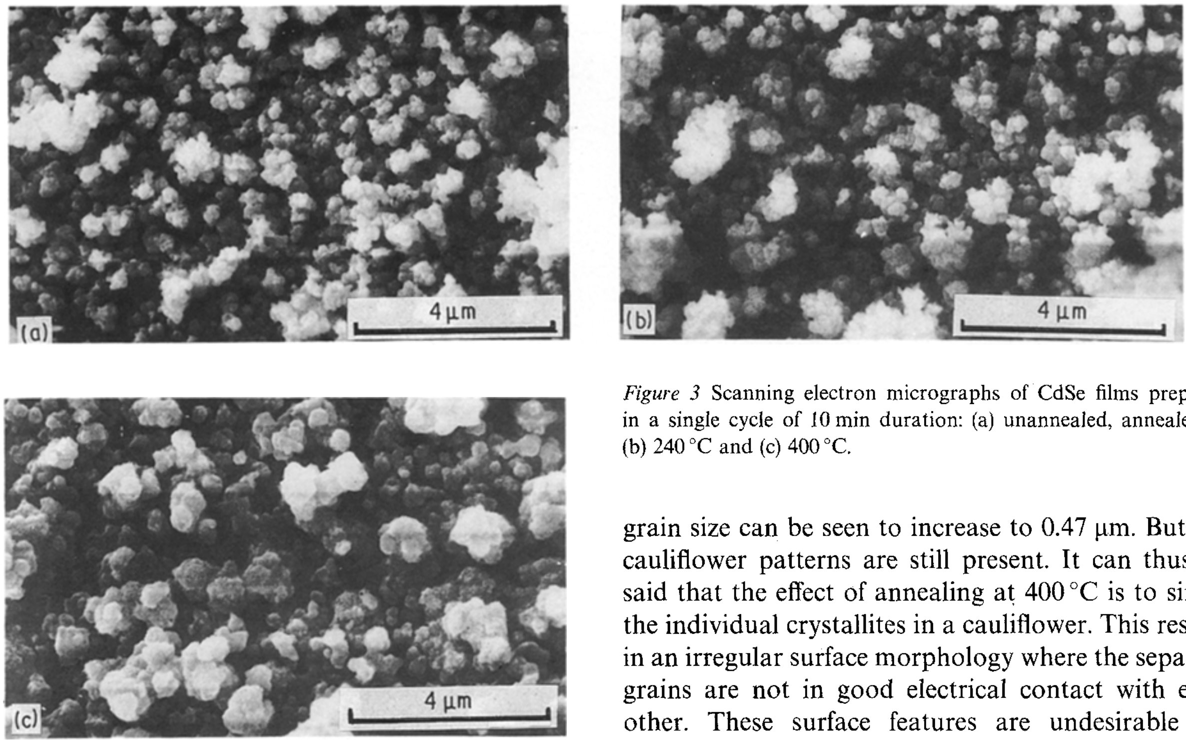

Figure 3 Scanning electron micrographs of CdSe films prepared in a single cycle of 10 min duration: (a) unannealed, annealed at (b) 240 °C and (c) 400 °C.

240 °C and above was found to be rich in cadmium. However, the bulk acquires a uniform composition with Se:Cd ratio of 1.0.

The surface morphology of the CdSe films electrodeposited in a single cycle of 10 min was examined by SEM. Fig. 3a–c shows the SEM photographs of the CdSe films in the as-deposited condition and after annealing at 240 and 400 °C, respectively. The porous nature of the unannealed CdSe film is obvious from the difference in contrast of the surface particles (in ligher contrast) which are in poor electrical contact with the bulk (dark contrast). The surface morphology resembles a cauliflower pattern, which is typical of the electrodeposited CdSe films. The surface features of the CdSe films after annealing at 240 °C were found to be similar to the as-deposited films. The particle sizes were similar in both cases. This indicates that the only process occurring during annealing at 240 °C is the removal of excess selenium from the bulk of the electrodeposit. The charging effects, however, can still be seen in Fig. 3b. Annealing at 400 °C reduced the charging as is evident from Fig. 3c. Also the average grain size can be seen to increase to 0.47 µm. But the cauliflower patterns are still present. It can thus be said that the effect of annealing at 400 °C is to sinter the individual crystallites in a cauliflower. This results in an irregular surface morphology where the separate grains are not in good electrical contact with each other. These surface features are undesirable for photovoltaic applications as they increase forward leakage current, grain boundary recombination and reduce the fill factor.

3.2. Three-cycle electrodeposited CdSe films

Fig. 4a and b shows SEM photographs of the CdSe films obtained after the first and second cycles of deposition followed by annealing at 340 °C. A fairly uniform distribution of grains can be seen in both cases. The average grain size of the CdSe films obtained after second cycle of deposition and annealing was 0.42 µm, which is nearly equal to the average grain size obtained in CdSe films deposited for 10 min using a single cycle of electrodeposition and annealing at 400 °C. Comparing Figs 4 and 3c, it can be said that a more uniform distribution of grains is obtained when a repeated cycle of electrodeposition is used to grow the CdSe films.

The surface morphology of the CdSe films obtained after three cycles of deposition and final annealing at 400 °C (film B) is shown in Fig. 5. This sample exhibited a more regular surface with well connected and larger grains. The charging effect observed in SEM

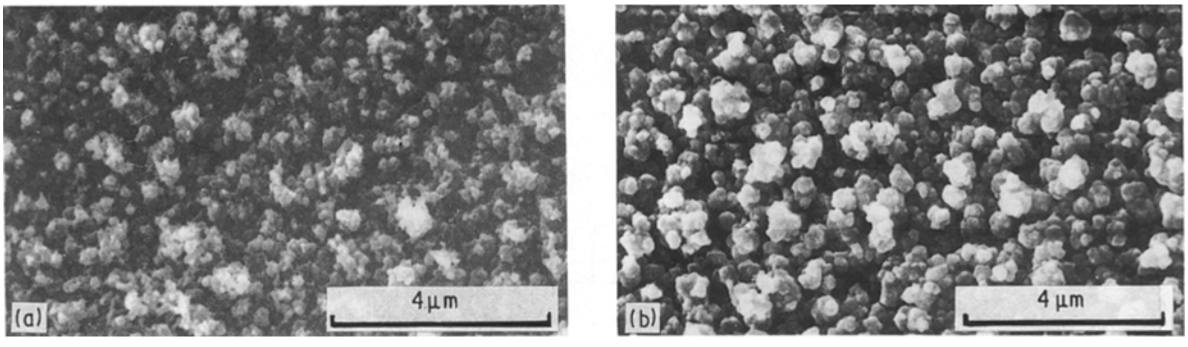

Figure 4 Scanning electron micrographs of CdSe film after (a) first and (b) second cycle of electrodeposition.

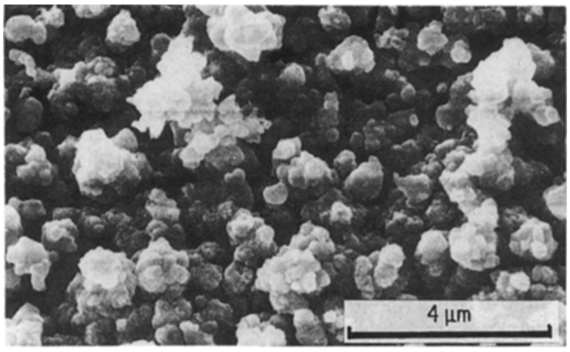

Figure 5 Scanning electron micrograph of a typical CdSe film prepared by three cycles of deposition and final annealing at 400 °C.

photographs of film A (Fig. 3c) is also considerably reduced. The average grain size in film B was 0.75 µm, as compared to 0.47 µm for film A.

The results of XRD analysis of the CdSe film grown using a single and three cycles of deposition are shown in Fig. 6. All the XRD peaks were identified and have been marked in the figure. The XRD data indicated that both the zinc blend (ZB) and Wurtzite (W) phases are present in the films. As shown in Table I, a reasonable agreement between the experimentally observed and standard *d* values was obtained for both the crystalline phases. The intensity ratio of the observed XRD peaks also agrees with the standard values given in the ASTM file [18]. The XRD peak intensities for the CdSe films deposited by adopting three cycles of electrodeposition were found to be higher than the corresponding peak intensities observed in the films deposited by a single cycle. The peak width at half maxima also increased in case of the former films as given in Table II. These trends indicate that the average grain size also increases in the CdSe films grown using three cycles of deposition.

4. Conclusions

From compositional analysis using AES, studies of surface morphology using SEM, and structural analysis using XRD, the following conclusions can be drawn.

1. The cathodic electrodeposition of CdSe films from an aqueous acidic bath often yields porous deposits. A possible reason for the porosity is the excess of elemental selenium in the film, which passivates the cathode surface.

2. The problem of the film porosity can be overcome by a repeated cycle of electrodeposition, annealing and *in situ* etching, as discussed in the present work. The CdSe films obtained by this technique were found to possess a more regular surface, and larger grains with no evidence of charging in the SEM photographs. The improvement in the crystallinity and surface morphology of the CdSe films obtained by the modified deposition technique can be ascribed to the following factors.

(i) The repeated cycle of deposition covers the micropores present in the parental CdSe layers. The annealing prior to the commencement of the next

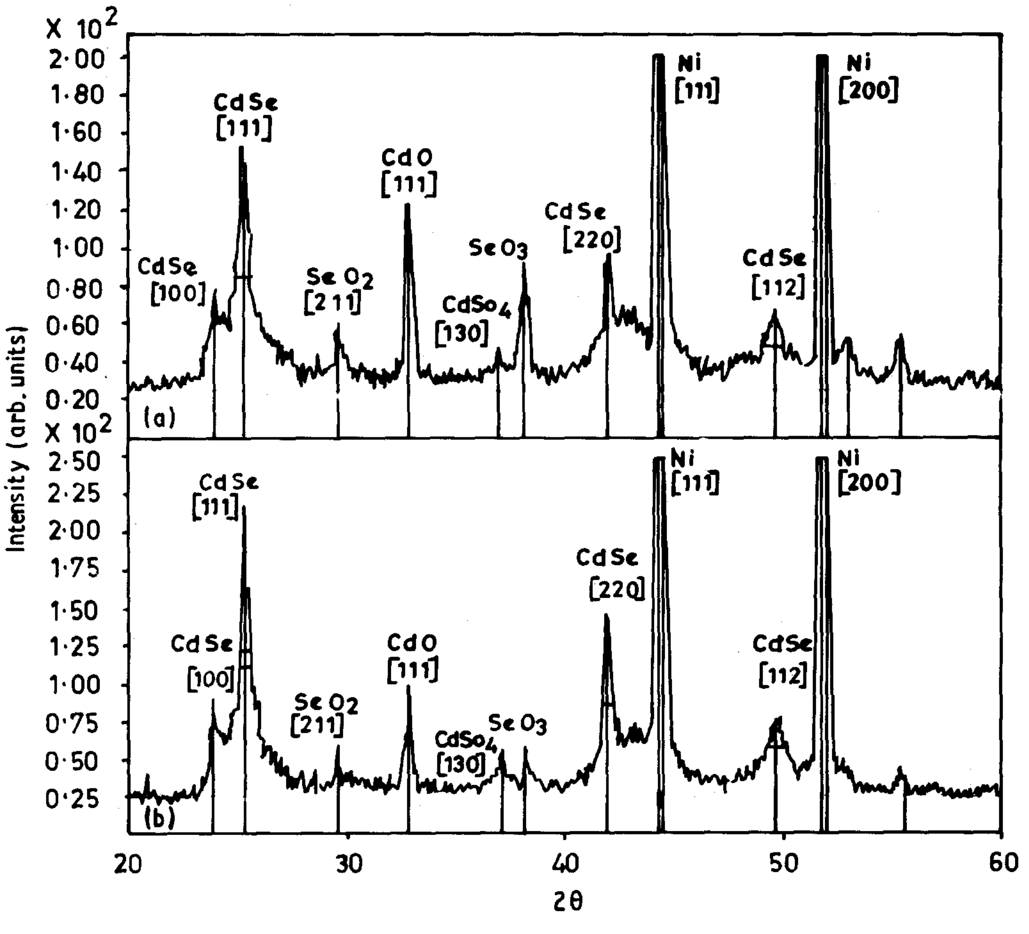

Figure 6 X-ray diffraction spectra of CdSe films deposited by (a) single and (b) three cycles of deposition and final annealing at 400 °C.

TABLE I A comparison of 2θ, d, relative peak heights and crystal phases of annealed CdSe film prepared by single and three cycles of deposition

Observed values						Reported values			
Film A			Film B						
2θ	d (nm)	Relative peak height	2θ	d (nm)	Relative peak height	2θ	d (nm)	Relative peak height	Crystal phase and Miller planes
24.047	0.3697	45	23.852	0.3727	66	23.891	0.3720	100	W(1 0 0)
25.472	0.3493	110	25.370	0.3507	185	25.344	0.3510	100	ZB(1 1 1)
42.052	0.2146	62	41.957	0.2151	106	41.992	0.2149	55	ZB(2 2 0)
49.790	0.1829	25	49.732	0.1831	46	49.649	0.1834	50	W(1 1 2)
55.302	0.1659	22	55.380	0.1657	10	55.820	0.1645	8	W(2 0 2)

TABLE II A comparison of peak width at half maxima (PWHM) for CdSe films A and B

Miller plane	CdSe Film A PWHM	d(nm)	CdSe Film B PWHM	d(nm)
1 1 1	0.75	0.3493	0.45	0.3507
2 2 0	0.75	0.2146	0.53	0.2151
1 1 2	1.06	0.1829	0.90	0.1831

TABLE III A summary of the V_{oc}, J_{sc}, fill factor, efficiency, donor concentration (N_D) and diffusion length (L_p) obtained from annealed CdSe films deposited using single and three cycles of deposition. The illumination level used for solar cell studies was 50 mW cm^{-2}

Fabrication history	V_{oc} (mV)	J_{sc} (mA cm^{-2})	Fill factor	Efficiency	N_D (per cm^3 × 10^{15})	L_p (μm)
Film A	470	8	0.38	3.6%	4.08	0.31
Film B	470	13	0.45	5%	1.87	0.47

deposition cycle removes excess selenium which may otherwise passivate the film surface. The *in situ* etching helps in removing any oxide layer and providing a fresh CdSe surface for the growth.

(ii) The grains of the parental CdSe films may act as nucleation centre for further growth during subsequent cycle of deposition. This will result in well connected and larger grains in the electrodeposits.

(iii) The improved crystallinity and surface morphology of the CdSe films resulting from the modified deposition technique are expected to improve the electronic properties of the film and eventually yield higher solar-cell efficiencies. This expectation was indeed vindicated by our results on the photoanodic performance of the CdSe film. Table III summarizes the performance of the electrochemical solar cells fabricated from CdSe films grown by the two techniques, and the sulphide–polysulphide redox couple. The experimentally determined values of minority carrier diffusion length and donor concentration in the two films are also shown in Table III. An all-round improvement in short-circuit current, fill factor, efficiency, L_p and N_D results when the CdSe films are grown by using three cycles of electrodeposition. Further work is in progress and will be the subject of future publications.

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References

1. G. HODES, J. MANNASEN and D. CAHEN, *Nature* **261** (1976) 403.
2. S. CHANDRA and R. K. PANDEY, *Phys. Status Solidi a* **59** (1980) 787.
3. R. B. GORE, R. K. PANDEY and S. K. KULKARNI, *J. Appl. Phys.* **65** (1989) 2693.
4. R. B. GORE, R. K. PANDEY and S. K. KULKARNI, *Solar Energy Mater.* **18** (1989) 159.
5. B. M. BASOL and O. M. STAFSUDD, *Thin Solid Films* **78** (1981) 217.
6. R. N. BHATTACHARYA and K. RAJESHWAR, *J. Appl. Phys.* **58** (1985) 3590.
7. M. P. R. PANICKER, M. KNASTER and F. A. KROGER, *J. Electrochem. Soc.* **125** (1978) 566.
8. R. N. BHATTACHARYA, K. RAJESHWAR and R. N. NOUFI, *ibid.* **131** (1984) 939.
9. G. HODES, J. MANASSEN and S. NEAGU, *Thin Solid Films* **90** (1982) 433.
10. G. HODES, T. ENGELHARD and D. CAHEN, *ibid.* **128** (1985) 93.
11. R. P. SINGH, S. L. SINGH and S. CHANDRA, *J. Phys. D: Appl. Phys.* **19** (1986) 1299.

12. F. J. PERN, J. GORAL, R. J. MATSON, T. A. GESSERT and R. NOUFI, *Solar Cells* **24** (1988) 81.
13. R. K. PANDEY and A. J. N. ROOZ, *J. Phys. D.* **19** (1986) 917.
14. R. K. PANDEY, A. J. N. ROOZ and S. K. KULKARNI, *Thin Solid Films* **150** (1987) 57.
15. P. W. PALMBERG, G. E. RIACH, R. E. WEBER and N. C. MacDONALD, "Handbook of Auger Electron Spectroscopy" (Physical Electronics Industries, Eden Prairie, Minnesota, Montana, 1972) p. 5.
16. R. B. GORE and R. K. PANDEY, *Thin Solid Films* **164** (1988) 255.
17. N. K. SKYLLAS and B. MILLER, *J. Electrochem. Soc.* **127** (1980) 869.
18. ASTM X-Ray powder data, 19–191 and 8–459.

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