

Comparative study of CdS thin films deposited by single, continuous, and multiple dip chemical processes

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Abstract

We have used Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), Raman, and photoconductivity to characterize CdS thin films grown by single, continuous, and multiple dip chemical processes. XRD has further shown, without ambiguity, that grown CdS films, independent of the process, in an almost homogeneous reaction free basic aqueous bath have a zincblende crystal structure where reflections from (111), (200), (220), and (311) planes are clearly identified. RBS, Raman, and photoconductivity confirm the high stoichiometry and excellent structural properties with low optically active trap state density of single and continuous dip CdS films. However, they collectively suggest that multiple dip CdS films suffer from defects that act as carrier traps and lead to prolong photoconductivity decay in these films. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Chemical bath deposition (CBD) is a method of growing thin film of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 100°C. It has been identified as one of the techniques for growing [1] polycrystalline and epitaxial CdS films at low cost. In CBD, two processes [1–4] are traditionally used for film growth: single dip, where the substrate is immersed in the reaction bath only once, and multiple dips, where the same substrate is repeatedly coated to obtain thicker film. Recently, we developed [2] a new process called continuous dip; here, the substrate that is being coated remains in the reaction bath while the reactants are periodically replenished in order to improve the quality or increase the thickness of the deposited film.

In our previous work [2] on the optimization of CBD grown CdS, we minimized a non-film forming reaction called homogeneous reaction. This reaction, if it predominates, is responsible for the formation of CdS colloids,

quickly depletes the reaction bath of useful reactants, limits the thickness of the deposited film, and eventually degrades the quality of the deposited film. In fact, it is the success in the drastic reduction of this reaction that has enabled us to grow CdS film by single, continuous, and multiple dip chemical processes with improved optical properties and dark resistivity ranging from 10^3 to $10^4 \Omega \text{ cm}$ without any postgrowth heat treatment.

CDB, apart from its low cost and capability to grow film over large area, produces CdS films with properties [5] highly suitable for thin film CdTe or Cu(InGa)Se₂ solar cells. The present efficiencies [6,7] of 15.8% of CdTe solar cells and 17.7% of Cu(InGa)Se₂ solar cells, which are in the league of best performing thin film photovoltaic cells, are achieved with CBD grown CdS films. In addition, a recent successful epitaxial growth of CdS [1] and CdSe [8] on single-crystal III–V compound substrates by CBD further raises the potential of this growth technique in the fabrication of optoelectronic devices.

Since various applications require various film grades, an introduction of continuous dip processed films thus expands our options. But an intelligent choice of CdS material for a given application must be based on at least the knowledge of composition, structure, and photoconductivity among other

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properties of the material. At present there is hardly any data on continuous dip CdS films. Therefore, in this paper we analyze and compare the properties of continuous dip process CdS films with those grown by single and multiple dip processes, using photoconductivity, Rutherford back-scattering spectrometry (RBS), Raman spectroscopy, and X-ray diffraction (XRD).

2. Experimental details

2.1. Synthesis

Reagents used for the deposition include cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), ammonium acetate ($\text{NH}_4\text{CH}_3\text{COO}$), ammonia water (NH_4OH), and thiourea ($\text{SC}(\text{NH}_2)_2$). All depositions were carried out on soda lime glass substrate using our previous [2] optimal growth conditions at 85°C , where $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]/[\text{NH}_4\text{OH}] = 0.0034$, and $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.06$. The concentration of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ selected for the experiment and the determination of concentrations of all other reagents is either 0.002 M or 0.005 M. For a given growth process, the choice of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ concentration (0.002 M or 0.005 M) and the subsequent concentrations of other reagents calculated from the optimum ratio quoted above have essentially no effect on the film properties. The detail procedures for the film growth are described in our earlier work [2]. The summary of these procedures and results is as follows:

1. In the case of single dip process where the substrate was coated only once, the thickness of the grown films ranged from about 0.04 to 0.5 μm . These films were grown at the rate of about 29 $\text{\AA}/\text{min}$.
2. For multiple dip process the substrate was coated at least two times and at most four times. The thickness yield after the first coating was found to be 100–120%. The thickness of the film grown by this process was between 0.15 and 2 μm .
3. In continuous dip deposition the reactant concentrations in the replenishing solution were the same as those in the initial cycle, except that of ammonium acetate which was changed. The ratio of $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ to $[\text{NH}_4\text{CH}_3\text{COO}]$ used in the replenishing solution in this study was 0.08. This gave the thickness yield of about 42% per cycle relative to that obtainable in a single dip. The cycle periods ranged from about 30 to 90 min. The grown film thickness was between 0.13 and 0.6 μm . The growth cycles, on the other hand, were at least two and at most six.

2.2. Characterization

2.2.1. Conductivity

Ohmic contacts were established by two coplanar In/Ag electrodes evaporated onto the surface of CdS film depos-

ited on soda lime glass substrate. The contact separation ranged between 10 and 13 mm. For the photoconductivity measurement, the prepared sample was connected to the input of a current controlled voltage source device based on a single operational amplifier in an inverting configuration. The bias voltage was 10 V and the feedback resistance 100 k Ω . The output voltage was measured as a function of time using a Tektronix 2211 digital storage oscilloscope. The sample was illuminated for about 150 s during each run with a 300 W General Electric light bulb. The intensity of light at the sample was maintained at 830 lux as measured by the fluxmeter.

2.2.2. RBS

The CdS thin films deposited on soda lime glass substrate were analyzed by RBS. 3.05 MeV α -particles was used as incident ions. A silicon surface barrier detector was used to obtain RBS spectra. The detector was located at 165° relative to the incident beam direction. The energy resolution of the detection system was 13 keV.

2.2.3. XRD

The crystalline structure of the films was analyzed using a Rigaku X-ray diffractometer with 1.5418 \AA Cu K_α line. The 2θ scan rate was 0.125 $^\circ/\text{min}$.

2.2.4. Raman

The Raman study was carried out with a confocal micro-Raman spectrometer. A 30 mW (3 mW at the sample), air-cooled argon-ion laser was used to excite the samples at 4880 \AA . A 200- μm aperture placed in the path of backscattered light blocked contributions from out-of-focus regions; providing axial resolution on the order of microns. A nitrogen-cooled, thinned, back-illuminated CCD detector recorded the spectra with 3 cm^{-1} resolution.

3. Results and discussion

3.1. RBS

Fig. 1 shows the typical raw RBS spectrum of CdS film grown by various processes on soda lime glass. In addition to Cd and S peaks, Si, O and Na signals are also observed. The Si, O, and Na signals are from the substrate. The IBM ion beam analysis software was used to analyze the acquired RBS data. Here, the near-surface absolute atomic concentrations of Cd and S were determined and the ratio of Cd to S calculated to determine the composition of CdS films. These calculations revealed that the near surface layer has, within the experimental error of about 3%, the ratio of Cd to S in single dip and continuous dip grown CdS films to be 1.00, whereas that of multiple dip films is 0.92. For continuous or multiple dip films the Cd to S ratio is independent of the number of cycles or dips as long as these are two or more. Previous work by Kylner et al. [9], however, showed that

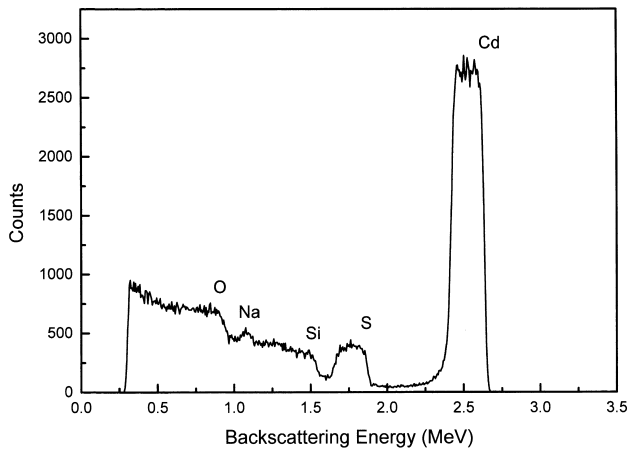


Fig. 1. Typical RBS spectrum of CBD grown CdS thin films on soda lime glass substrate.

CBD-CdS films have Cd to S ratios ranging from 1.02 to 1.08. The minor contrast in these results may be due to the fact that the latter did not use ammonium salt in their deposition. This salt is known [2] to provide more NH_3 which helps bind Cd^{2+} into a complex ion and reduces OH^- which eventually reduces the release of S^{2-} and consequently slows the growth rate; a necessary and sufficient condition to have a stoichiometric growth. As a result, Kylner et al. [9] ended with a higher growth rate; their maximum growth duration was about 8 min in single dip deposition as against 0.5 to 4 h in our case. We therefore infer that the similarity in the ratio of Cd to S, 1.00, in our single dip and continuous dip CdS films is due to low growth rate which insures that the growth environments of these films are basically the same. Several researchers [2,3] have observed, in CBD multiple dip deposition, that when there is an initial film layer on a substrate, subsequent film layers grow at a faster rate. The slight deviation from stoichiometry in our case, for multiple dip films, and that reported by Kylner et al. [9], for both single and multiple dip films, point to the fact that fast growth rate in CBD encourages the deviation of Cd to S ratio from one. The direction of deviation of this ratio, however, depends on the growth conditions, which can sometime encourage excess S or Cd.

3.2. XRD

The XRD of various samples of CdS films independent of whether the film was grown by single, multiple, or continuous dip chemical process gave diffractogram of similar appearance. However, to prevent the burying of CdS XRD peaks in the glass broad X-ray spectrum, the thickness of the films studied was at least 2500 Å. Fig. 2 shows the typical XRD pattern of as-grown CdS film on soda lime glass. The 2θ values of diffraction peaks observed are 26.5, 30.8, 43.9, and 52.1°; these correspond [10,11] to reflections from (111), (200), (220), and (311) planes of cubic (zincblende)

CdS, respectively. The reflections from these planes have previously been reported [12] for CBD-CdS films grown on Si(111) substrate from a similar bath. De Melo et al. [13] also observed reflections from these planes but (200) plane for CBD-CdS film grown on glass. It is known [14–16] that CdS structure has a stable hexagonal phase and a metastable cubic phase. For a basic aqueous chemical bath grown CdS films, Zelaya-Angel et al. [14,15] did show that the CdS film as grown has a cubic structure and the transition from this metastable phase to the stable hexagonal phase occurs around 300°C. The quick inference from all these observations is that the mechanisms of CdS film growth in a basic aqueous chemical bath favors a cubic structure formation; more so that the growth temperatures, ranging from room temperature to 100°C, are much lower than this transition temperature. However, several other authors [4,11,17] classified the structure of as-grown CBD-CdS film from a basic aqueous bath as hexagonal. In the reports [4,11] where this claim is backed up by the XRD pattern of the CBD-CdS film, a single reflection peak located at 26.5° which as a matter of fact could have emanated from the (111) plane of cubic or (002) plane of hexagonal CdS structure, is observed. Based on the findings of Zelaya-Angel et al. [14,15], Lincot et al. [12], our present result, and other investigations carried out by us [18], we attribute this latter reflection to that of (111) plane of a cubic CdS. Further, we state that CBD-CdS film as grown from a basic aqueous bath has a zincblende structure and the type of substrate or growth condition determines the number of XRD reflection peaks. But in this study all our films independent of growth processes gave reflection from four planes, as against three [13,15] and one [4,11] that were previously reported for CBD-grown CdS film from a similar bath on the glass substrate. Nevertheless, as our dominant reflection is also along the axis perpendicular to the (111) plane parallel to the substrate surface as reported by these authors, we can infer in this case that the growth originated from nucleation processes [4,11]. In addition, the trend in intensity of these peaks follows that of the standard [10,11,19] CdS powder

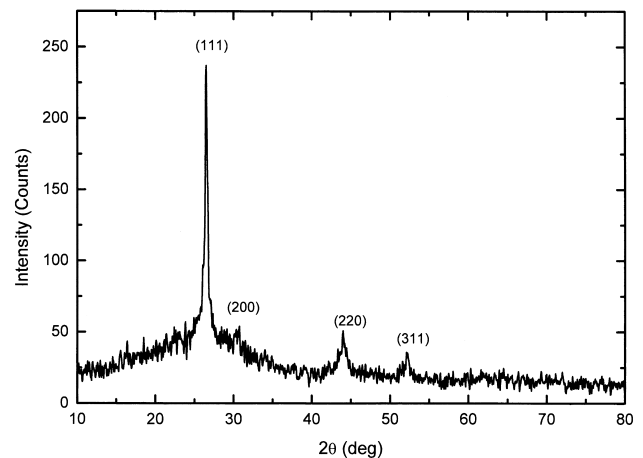


Fig. 2. Typical XRD pattern of CBD-CdS thin film as grown.

diffraction, thereby testifying to the quality and polycrystallinity of our films.

3.3. Raman

Fig. 3a–c show the typical Raman spectra of CdS thin films grown by continuous dip, single dip, and multiple dip processes respectively. Each spectrum has at least three peaks. These peaks can be identified as the multi-overtones of the longitudinal optical (LO) phonons by comparing with CdS Raman spectra obtained by previous workers [20,21]. The spectra show that there are four Raman peaks from films deposited by continuous dip in contrast to three from single and multiple dip films. These Raman spectrum profiles are independent of thickness ranging from 0.04 to 2 μm , and in the case of multiple or continuous dip films are essentially independent of the number of dips or cycles as long as this number is at least two. For completeness, Table 1 shows the comparison in wavenumber, of LO modes of our films with those of single-crystal [20] CdS and pulsed laser-evaporated [21] (PLE) CdS thin films that are also excited by the 4880 \AA argon-ion line at room temperature. Here, the wavenumbers of LO modes of our films, like those of LPE CdS films, shifted slightly to lower values compared to single-crystal LO modes. These shifts, according to Chuu et al. [21], are due to the small dispersion of LO mode phonon wave vectors in polycrystalline films.

Let us consider for a moment the dominant 1LO mode in the CBD-grown CdS films. The wavenumber of this mode within the experimental error that is less than 1% is 303 cm^{-1} in continuous dip films and 299 cm^{-1} in both single

Table 1

Comparison in wavenumber of LO modes of our films with those of single-crystal CdS and pulsed laser-evaporated (PLE) CdS thin films excited by 4880 \AA argon-ion line at room temperature

CdS type or growth method	Raman shift (cm^{-1})			
	1LO	2LO	3LO	4LO
Single crystal [13]	305	604	909	1200
PLE [14]	300	600	904	–
Continuous dip	303	600	899	1190
Single dip	299	597	900	–
Multiple dips	299	595	903	–

dip and multiple dip films, where 2 and 6 cm^{-1} are respective shifts from 305 cm^{-1} of the single-crystal CdS. The 1LO in continuous dip film has the least shift, indicating that this film has a better structure. However, the 1LO of the multiple dip film with a larger shift appears to be asymmetric. The peak asymmetry in the latter is known [1] to result from high density of stacking faults, leading us to conclude that multiple dips CdS films have an inferior quality; more so that the overall intensities of the peaks of these films are weaker than those of single and continuous dip films. Though the shift of 1LO in single dip film is large, unlike the multiple dip film it is symmetric, meaning that it has a structural quality comparable to that of continuous dip film.

X-ray analysis shows that CBD-grown CdS films, independent of growth technique, has a zincblende polycrystalline structure with grain sizes of the order of 500 \AA . Though Raman analysis does not generally distinguish between zincblende and wurtzite structures [22] of CdS, it has in this case, as in the past, shown subtle variations in the structure of our films. Also, from the Raman spectra the full width at half maximum (FWHM) of 1LO peaks are 18, 19, and 20 cm^{-1} for continuous dip, single dip, and multiple dips CdS films respectively. The values previously reported [1] for cubic CBD-CdS film range from 20 to 30 cm^{-1} . Our values agree with the low end of this latter range, thus attesting to the quality of our films.

3.4. Photoconductivity

It is known [23] that defects or impurities acting as electron trap states in II–VI compounds set a limit to the performance of these materials as photoconductors. Poor performance [23,24] as a result of high density of trap states, especially at low excitation intensities, includes among others a slow response time and at all levels of excitation a long decay time. An accurate and explicit determination of response and decay times in wide band-gap II–VI compounds, in most cases, is almost impossible [24]. This is because they are affected by many factors and controlled by different mechanisms that lead to a non-exponential behavior of photocurrent/time relation; also observed in this study. For simplicity, therefore, we will only present a

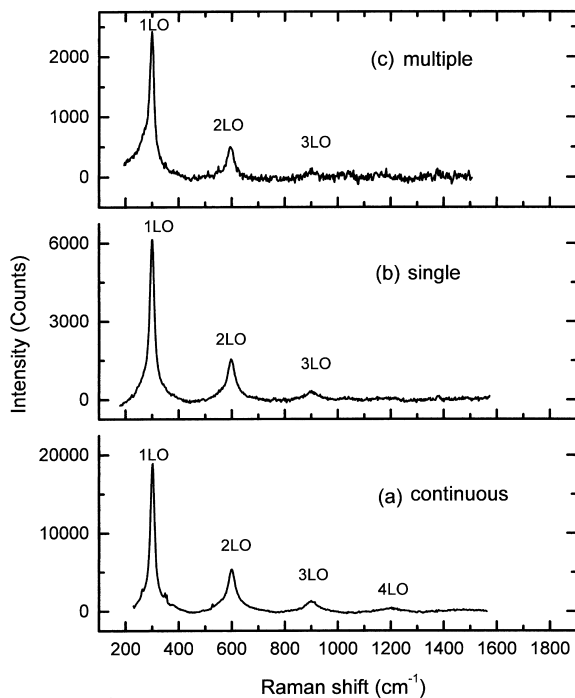


Fig. 3. Raman Spectra of CdS thin films grown by (a) continuous, (b) single, and (c) multiple dip chemical processes.

qualitative description of photocurrent/time relation of our films; a presentation that is similar to what was previously done by Nair et al. [25,26].

Fig. 4 shows the typical photocurrent of our CdS thin films of 0.5 μm average thickness grown under various processes before, during, and after exposing them to a low intensity (830 lux) white light. In single dip CdS film, Fig. 4b, at illumination the photocurrent rises sharply, saturates rather quickly, and falls off rapidly to the dark current value when the light is turned off; whereas for multiple dip films, Fig. 4c, the photocurrent rise is not as fast, has not saturated after about 150 s of illumination, and post-illumination the current still persists, even 300 s after. The photocurrent behavior in continuous dip film, Fig. 4a, on other hand, is in between that of multiple dip and single dip films, but closer to the latter. For each growth process, the photocurrent rise and fall profiles remain essentially the same. However, the peak photocurrent in the same class of films depends on the film thickness.

Generally, trap states that trap holes during photocurrent rise help prolong the lifetime of electrons in the conduction band, resulting in a net increase in photocurrent, but they are notorious in delaying the fall of the latter unnecessarily as observed in some films. Also, high density of recombination centers in the bulk and surface of a material reduce the lifetime of carriers and consequently current, and shortens the photocurrent rise and fall times. From the description above and the observed peak photocurrents of our films, as shown in Fig. 4, it could be inferred that recombination [24] in the single dip CdS films is dominated by recombination

centers, whereas in multiple dip films by trap states, and in continuous dip films by both. All the grown CdS films are polycrystalline as shown by XRD. Since the single dip CdS films have the simplest growth conditions and have excellent qualities as shown by RBS and Raman but low peak photocurrent and fall time, we can possibly say that the dominant recombination centers here are the grain boundaries of the polycrystalline films. In multiple dip CdS films, RBS has detected a Cd to S ratio of 0.92, and the Raman spectrum suggests the presence of high stacking fault possibly at the interface of subsequent layers of these films. The combination of these anomalies may perhaps be the source of the high optically active carrier trap density and the accompanying pronounced transient photocurrent. However, the periodic replenishing of reagents in continuous dip films may have introduced certain defects undetected by RBS and Raman that also serve as trap states. The density of these states being low here or the carrier trap mechanisms being different may explain why we have a smaller fall time and peak photocurrent compared to those observed in multiple dip CdS films.

4. Conclusion

X-ray diffraction results have further confirmed that CdS films grown by CBD in a basic aqueous bath independent of the growth process in an almost homogeneous free reaction bath has a cubic structure. RBS and photocurrent studies have revealed that continuous dip CdS films have properties comparable to that of single dip CdS films. Raman has shown that continuous dip films have structure superior to those of single and multiple dip CdS films. Multiple dip CdS films, however, have the highest peak photocurrent owing to trap states that trap holes and help prolong the electron lifetime in the conduction band.

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References

- [1] M. Froment, M.C. Bernard, R. Cortes, B. Mokili, D. Lincot, J. Electrochem. Soc. 142 (1995) 2624.
- [2] I.O. Oladeji, L. Chow, J. Electrochem. Soc. 144 (1997) 2342.
- [3] R. Jayakrishnan, S.R. Kumar, R.K. Pandey, Semicond. Sci. Technol. 9 (1994) 97.
- [4] J.M. Dona, J. Herrero, J. Electrochem. Soc. 139 (1992) 2810.
- [5] R. Ortega-Borges, D. Lincot, J. Electrochem. Soc. 140 (1993) 3464.
- [6] C. Ferekides, J. Britt, Y. Ma, L. Killian, Proc. 23rd IEEE Photovoltaic Specialists Conference, 1993, p. 389.
- [7] R.N. Bhattacharya, N. Batchelor, H. Wiesner, J. Electrochem. Soc. 145 (1998) 3435.

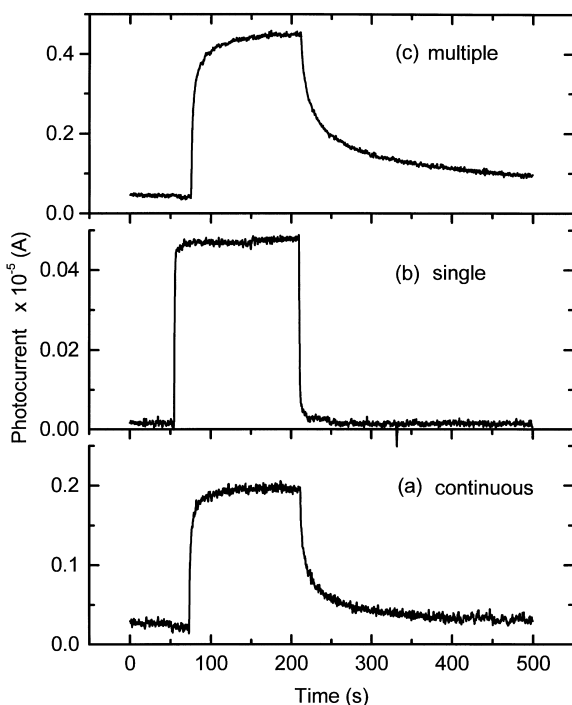


Fig. 4. Photocurrent rise and fall of CdS thin films grown by (a) continuous, (b) single, and (c) multiple dip chemical processes.

- [8] H. Cachet, R. Cortes, M. Froment, G. Maurin, N. Shramchenko, J. Electrochem. Soc. 144 (1997) 3583.
- [9] A. Kylner, J. Lindgreen, L. Stolt, J. Electrochem. Soc. 143 (1996) 2662.
- [10] JADE 3.0 database, PDF card #10-0454.
- [11] T.L. Chu, Thin Film Cadmium Telluride, Zinc Telluride, and Mercury Zinc Telluride Solar Cells, NREL final subcontract report, # XL-8-18091-1 (1992).
- [12] D. Lincot, B. Mokili, M. Forment, R. Cortes, M.C. Bernard, C. Witz, J. Lafait, J. Phys. Chem. B 101 (1997) 2174.
- [13] O. De Mello, L. Hernandez, O. Zeleya-Angel, R. Lozada-Morales, M. Becerril, E. Vasco, Appl. Phys. Lett. 65 (1994) 1278.
- [14] O. Zeleya-Angel, F.L. Castillo-Alvarado, J. Avendano-Lopez, A. Escamilla-Esquivel, G. Contreras-Puente, R. Lozada-Morales, R. Torres-Delgado, Solid State Commun. 104 (1997) 161.
- [15] O. Zelaya-Angel, J.J. Alvarado-Gil, R. Lozada-Morales, H. Vargas, A. Ferreira da Silva, Appl. Phys. Lett. 64 (1994) 291.
- [16] O. Trujillo, R. Moss, K.D. Vuong, et al., Thin Solid Films 290–291 (1996) 13.
- [17] I. Kaur, D.K. Pandya, K.L. Chopra, J. Electrochem. Soc. 127 (1980) 943.
- [18] I.O. Oladeji, Ph.D. dissertation, University of Central Florida, Orlando, May 1999.
- [19] N.T.S. Nair, P.K. Nair, R.A. Zingaro, E.A. Meyers, J. Appl. Phys. 75 (1994) 1557.
- [20] R.C.C. Leite, S.P.S. Porto, Phys. Rev. 17 (1966) 10.
- [21] D.S. Chuu, C.M. Dai, W.F. Hsieh, C.T. Tsai, J. Appl. Phys. 69 (1991) 8402.
- [22] D.R.T. Zahn, C.H. Maierhofer, A. Winter, M. Reckzügel, R. Srama, A. Thomas, K. Horn, W. Richter, J. Vac. Sci. Technol. B 9 (1991) 2206.
- [23] B. Ray, II–VI Compounds, Pergamon Press, New York, 1969.
- [24] N.V. Joshi, Photoconductivity: Art, Science, and Technology, Marcel Dekker, New York, 1990.
- [25] P.K. Nair, J. Campos, M.T.S. Nair, Semicond. Sci. Technol. 3 (1988) 134.
- [26] P.K. Nair, M.T.S. Nair, Solar Cells 22 (1987) 103.