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FINAL REPORT

NASA Research Grant No. NAG3-1692

for the period

January 23, 1995 to April 22, 1995

Theoretical and Experimental Research in Space Photovoltaics: Electrodeposition of $CuIn_xGa_{1-x}Se_2$ (CIGS) Thin Layers for CdS/CIGS Solar Cell Applications

Submitted to

NASA Lewis Research Center

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Cleveland State University

Electrical Engineering Department, Space Photovoltaic Research Center

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Report prepared by the Principal Investigator

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I. Introduction

Under a NASA-Lewis Research Center grant (No. NAG3-658), for a period of three months covering October 1, 1994 through December 31, 1994, the research group at CSU has conducted theoretical and experimental research on "Electrodeposition of $CuIn_xGa_{1-x}Se_2$ (CIGS) Thin Layers for CdS/CIGS Solar Cell Applications." The main results are outlined below.

1. Background

The US. Department of Energy (DOE) and a segment of the photovoltaic industry have targeted photovoltaic (PV) modules based on thin films as likely candidates for low cost energy production [1-21]. Contributing factors include:

- the low materials cost for these thin films
- potential scalability and automation of the fabrication processes, and
- efficiencies that are competitive with the dominant single crystal Si-based technology.

The present economics of PV thin films do not support an easy transition to successful commercialization. This is because thin films have been developed as a means of reducing the cost of PV to compete for large power markets. However, the initial entry of thin films is at much higher prices that cannot yet compete for these presumed large markets. The problem is that the initial production of thin films occurs at:

- lower than expected efficiencies (due to relative immaturity of manufacturing capability), and
- at low volumes that fail to take advantage of economies-of-scales.

For certain space missions, such as a Lunar or a Mars base, there is a need for low cost high specific power solar cell arrays with reasonably high beginning-of-life efficiency, high stability, and high radiation resistance. Of these requirements, any potentially viable technology must satisfy the following three requirements right now, at the start, namely, low cost, high stability and high radiation resistance. Performance improvements can then be made in the near future, by doing the necessary research and development, so as to satisfy the remaining requirements of reasonably high efficiency and high specific power. Of the existing solar cell technologies, the polycrystalline thin film solar cell technology already satisfies these three requirements at the present time and, in addition, shows promise for satisfying the remaining two requirements of high efficiency and high specific power in the near future. Hence, it is our opinion that the polycrystalline thin film solar cell technology has the highest potential and shows the greatest promise of satisfying all of the above requirements for being a viable power technology for certain space applications.

The two most mature polycrystalline thin film solar cell technologies at the present time are the CdS/CdTe and CdS/$CuInSe_2$ (CIS) solar cell technologies. Of these, cells based on $CuInSe_2$ (CIS) show a better promise for reaching the goal than the CdTe-based cells. Polycrystalline thin film cells based on CIS have shown an efficiency of 15.4% at AM1.5, 25 C. A well-known approach to improve the performance of CIS-based solar cells is to replace some of the In with Ga (e.g. by alloying $CuInSe_2$ with $CuGaSe_2$ to form $CuIn_xGa_{1-x}Se_2$ (CIGS)), thus increasing the bandgap so as to obtain a better match to the sunlight spectrum. Recently, some excellent performance results have been reported for ZnO/CdS/$CuIn_xGa_{1-x}Se_2$ cells (15.9%, total area, AM1.5, 25 C) [4], with the n-CdS layer grown from an aqueous solution and the n - ZnO and p-$CuIn_xGa_{1-x}Se_2$ layers made by vacuum evaporation.

Recent efforts in polycrystalline thin film solar cell development have concentrated on the fabrication of large area devices using simplified low-cost processing techniques, while, at the same time, improving yield and performance. Presently developed fabrication technologies of thin film layers include epitaxy (MBE and MOCVD), elemental vacuum co-evaporation, close-spaced sublimation, screen-printing, spray pyrolysis and electrodeposition and electrodeless deposition from aqueous baths. In all of these technologies, significant improvements in cost reduction and throughput are necessary for them to become viable technologies for the low cost large scale production of polycrystalline thin film solar cells.

2. High Efficiency CIGS Solar Cells

Using physical vapor deposition methods small area CdS/CIGS cells with AM 1.5, 25 ^oC efficiency as high as 16.9% (J_{sc}=35.8 mA/cm^2; V_{oc}= 641 mV; FF= 73.5%) have been demonstrated [2]. Although for several small area cells some excellent performance results are seen, the manufacturability issues humble the very promising CIGS large area large scale development. In all of these technologies, significant improvements in cost reduction and throughput are necessary for them to become viable technologies for the low cost large scale production of polycrystalline thin film solar cells. To prove this point it is sufficient to examine the complexity of the fabrication process used for the above mentioned small area cell: soda-lime float glass substrate (0.8 mm) / Mo {800 nm, Sheet Resistance: 0.2-0.3 Ω/sq.; deposited by rf argon sputtering} / $Cu(In,Ga)Se_2$ {3 μm, co-evaporated from elemental sources controlled by a quadruple mass-spectrometer feedback system} / CdS { buffer layer; ~ 20 nm; deposited by solution growth using cadmium salt and thiourea [6]} / ZnO {window layer; First layer (~ 50 nm) high resistive ZnO deposited by rf magnetron sputtering from ZnO in Ar:1% O_2; Second layer (300 nm): ZnO:Al was deposited by rf magnetron or diode sputtering} / Front contacts: thin intermediate Ni layer and Al (~ 2 μm) / AR coating: MgF_2. Annealing: 200 ^oC, for 2-10 min in air.

Note: A CIS cell structure (similar fabrication, except that the oxygen concentration during the deposition of the first ZnO layer was 20%) have yielded an efficiency of 15.4% (AM 1.5, 25 ^oC) (J_{sc}=41.2 mA/cm^2; V_{oc}=515 mV; FF=72.6%).

Improvements in cost and throughput are necessary for large scale production. Recent efforts in large-area CIS and CIGS cells development are focusing on simplified, low-cost processing options with improved yield and performance. It is our opinion that of the most promising options are electrodeless and electodeposition solution growth of all active layers of the cell.

3. Chemical Bath Deposition

The CdS chemical bath deposition (CBD) process was developed by Chu et al., of Univ. of South Florida [7]. A cadmium salt, an ammonium salt, ammonia, and thiourea were the reactants used in an aqueous solution. The cadmium salt [e.g. $CdSO_4$ or $Cd(NH_3)_4{}^{2+}$] and thiourea [$CS(NH_3)_2$] are the source of Cd^{2+} and S^{2-} ions respectively, while ammonia (NH_4OH) serves as a buffer. The amount of ammonia and ammonium salt in the solution can be adjusted to control the deposition rate of the CdS films. The solution temperature also affects the deposition rate. Two groups of salts, the acetates and chlorides, can be used in the temperature range of 70-90 ^{o}C.

For CdTe/CdS and $Cu(In,Ga)Se_2$ thin film solar cells, the highest efficiencies for both these cell structures [2,7] have been achieved with CdS films prepared by this deposition technique. For CdS/CdTe solar cells with the CdS layer grown by the chemical bath deposition method and the CdTe layer grown by close-spaced sublimation (CSS), a record high efficiency of 15.8% (AM1.5, 25 C, 1.05cm^2 total area) has been achieved [5] with V_{OC} = 843mV, J_{SC} = 25.1 mA/cm^2 and FF = 74.5% (NREL data). The reason why CBS grown CdS gives better photovoltaic performance as compared to, e.g., evaporated CdS remains unclear. It has been suggested that (i) a pinhole-free conformal coverage, (ii) low temperature deposition, or (iii) the chemical treatment of the surface during the CBD process are of importance, but clear evidence has not been submitted.

Cadmium Free Buffer Layers for CIGS Cells

Several attempts have been made to replace the CBD grown CdS with other materials in using either a chemical bath deposition (CBD) or electrochemical process, but in all cases the standard CBD-CdS growth recipe lead to superior solar cell characteristics, mainly due to better values of the fill factor (FF) and the open circuit voltage (V_{OC}).

Recently, however, a new chemical bath process has been reported for the deposition of a buffer layer containing In, S and O [22], which has resulted in CIGS solar cells with performances comparable (nearly 15% efficiency) to those using the CBD-CdS buffer layer.

The deposition was carried out in an aqueous $InCl_3$ and thioacetamide (CH_3CSNH_2) solution at temperatures up to 70^{o}C. The suggested reaction paths during the deposition are shown in Figure 1.

Thioacetamide is known to decompose in aqueous solution at higher temperatures to ammoniaacetate and H_2S. For In^{3+}(aq) two reaction paths are possible:

1. The hydrolysis to $In(OH)_3$ is forced by heating aqueous In^{3+} solutions in the presence of ammoniumacetate.
2. In^{3+}(aq) can react with H_2S to form In_2S_3.

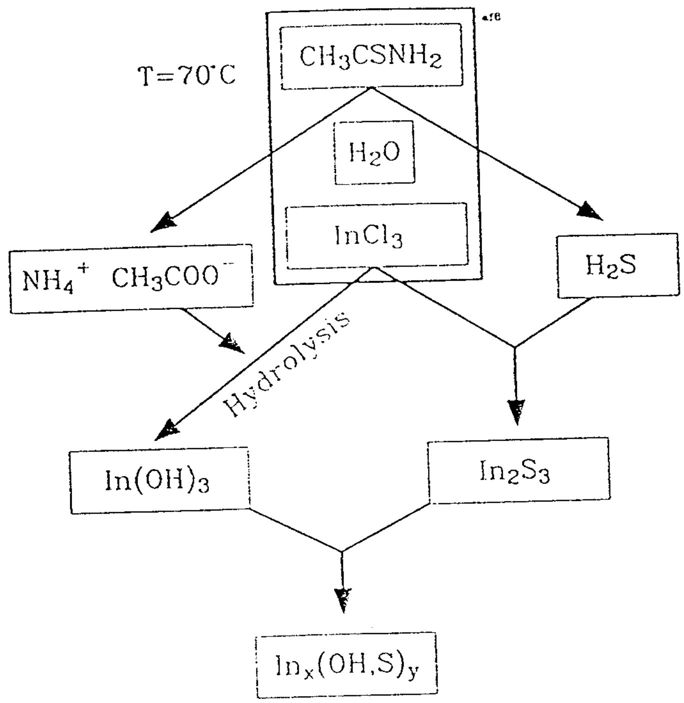

Figure 1. Schematic representation of the different possible reaction paths leading to the formation of $In_x(OH,S)_y$ buffer layer compound.

4. Electrodeposition

The electrodeposition technique is currently favored for the deposition of thin CdTe and $Cu(In,Ga)Se_2$ films with respect to large area processing, low cost, and high material yield. In addition, from the point of view of safety, in comparison to other thin film deposition techniques, electrodeposition has the major advantage of containing the component elements of the film in aqueous solutions; this makes for easy containment and safe handling and disposal.

4.1. CdTe Solar Cells

Since Panicker et al. [24] laid the foundation for electroplating CdTe thin films, various groups have worked on the technique to produce CdS/CdTe solar cells.

CdS/CdTe cells with both CdS and CdTe layers fabricated by electrodeposition have been proposed by Morris and Das from Univ. of Queensland, Australia [8]. CdS was electrodeposited from a 90 ^{o}C stirred solution in which the electrolyte was 0.2 M Cd^{2+}, and 0.01 M $S_2O_3^{2-}$ with the pH adjusted to 2 [20]. The deposition potential was + 40 mV from the measured cadmium deposition potential, and the growing rate was ~ 50 nm/hour. CdTe films were electrodeposited on $CdCl_2$ treated and untreated CdS films using an electrolyte based on 2.5 M Cd^{2+}, 120 ppm $HTeO_2^{+}$ and a pH of 1.7 [21]. The growth rate at 90 ^{o}C was ~1 μm/hour. The maximum AM1 efficiency obtained for the first cells of 10.2% (V_{OC}=753 mV; J_{SC}=20.6 mA/cm^2, and FF=66%) is very encouraging, when compared to similar cell structures fabricated by more sophisticated techniques.

Using electrodeposited CdTe thin films, the BP group has demonstrated large area (706 cm^2 aperture area) CdTe/CdS module with an AM1.5 global spectrum at 100 mW/cm^2 efficiency of 10.1% [20]. The CdS layer was grown using the chemical bath deposition (CBD) process [7].

4.2. CIS (CIGS) Solar Cells

For $CuInSe_2$ (CIS) cells, until yet, electrodeposition has given rather poor results. To our knowledge, $CuInSe_2$ films with electronic properties suitable for solar cells were first electrodeposited recently by reducing copper (II), selenium (IV) and indium (III) species in acidic solution at a potential value of -0.7 V to -1.1 V/MSE [23]. The composition of this films was controlled by the ratio between Cu (II) and Se (IV) fluxes at the electrode surface ($\alpha = J_{Se}/J_{Cu}$, Figure 2). For $\alpha<2$ the film is cooper rich and for $\alpha>2$ the film becomes indium rich in a large range of deposition potential.

Mo/CIS/CdS/ZnO solar cell structures with an electrodeposited CIS layer had a maximum efficiency of 6.5%. The relatively low efficiency of these cells as compared to evaporated cell structures is mainly related to losses at the CIS/CdS interface rather than to bulk properties of the CIS film.

Surprisingly, the published literature shows no reported data on the electrodeposition of CIGS thin film layers. Our preliminary study of the precursors for such growth shows that in principle, these layers could be grown by electrodeposition from non-aqueous solutions.

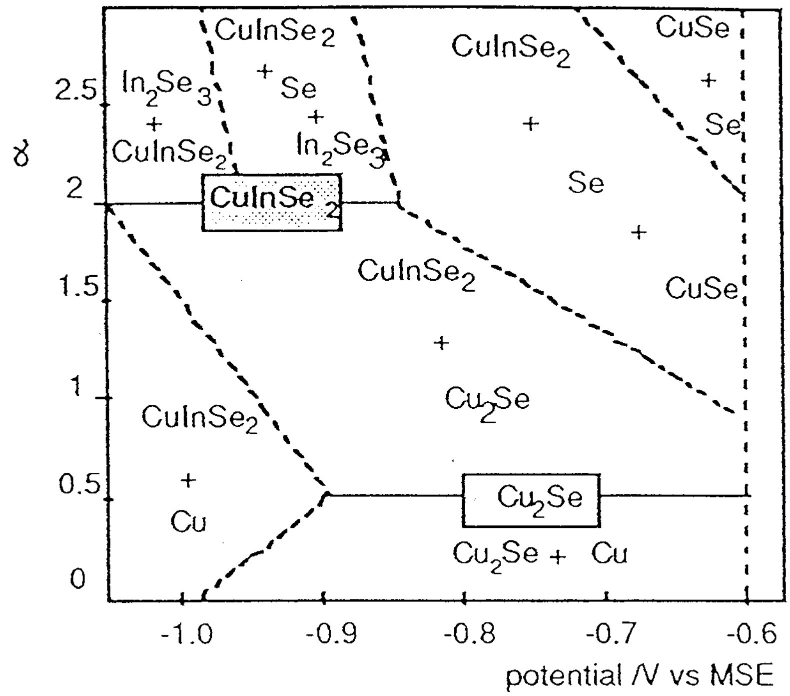

Figure 2. Qualitative phase diagram of electrochemically deposited compounds in the Cu-In-Se system.

II. Experimental Work

The objective of our experimental work was to develop a reproducible process for the electrodeposition of $CuIn_xGa_{1-x}Se_2$ (CIGS), CdS and ZnO thin film layers on silica or kapton substrates and to demonstrate the applicability of this process for the low cost, high throughput fabrication of high efficiency CdS/CIGS solar cells for space applications. The above was the overall objective of a two to three year research project of which only the proof-of-concept fabrication process development of solution grown (electrodeposited) CdS/CIGS structures were attempted during the three month period of this grant.

The proposed cell structure is: molybdenum/cooper (back contact) coated glass or kapton substrates/p-$CuIn_xGa_{1-x}Se_2$(CIGS)/n-CdS(buffer layer)/ n-ZnO (window layer)/MgF_2 (AR coating) with Ni-Al front grids. In our approach, all active layers of the cell: p-$CuIn_xGa_{1-x}Se_2$(absorber layer)/n-

CdS(buffer layer)/n-ZnO(window layer) are deposited using low temperature wet chemical or electrochemical methods.

Electrodeposition

Much work has been done on electrodeposition of thin films metals on semiconductor surfaces. In principal, the codeposition of two metals is the same as the deposition of a single metal, whereby the passage of a high current density in a bath of the mixed metallic salts will result in a deposit of two or more metals (e.g., Cu, Ga and In). Unfortunately, deposits obtained under high current density are loose, porous, nonadherent, and in most cases, compositionally inhomogeneous.

To codeposit two metals effectively, conditions must be optimized for depositing the less-noble metal without employing an excessive current density. Codeposition can be produced using either potential or current control. Under potential control, the composition of the deposit can be controlled precisely, although deposition rates are quite low. Conversely, current control promotes higher deposition rates, but deposition quality (composition) can be difficult to control. Regardless of the control method selected, however, a major limiting factor to deposition rate and overall thickness is depletion of the boundary layer near the solution/film interface. To overcome this, pulse plating techniques could be employed to improve adherence, deposition rates and deposit quality.

To codeposit two metals effectively, conditions must be optimized for depositing the less-noble metal without employing an excessive current density. For this, we first started a preliminary experimental study on single component metal electrodeposition on molybdenum coated silicon substrates. All electrodepositions experiments were performed at room temperature without stirring. Within our preliminary work the best deposits we obtained using the solutions in Table 1:

For convenience, for these experiments we used 2" p-Si wafers, with Al evaporated on the back surfaces. After sintering the Al back contacts, Mo was plated on the mirror-like front surfaces, at a current density of 3 to 10 mA/cm^2. Although not very uniform, the best deposit was obtained at a current density of about 6 mA/cm^2. After Mo plating, the Si wafers were cut into smaller size samples, which we used for plating Cu, In and Se.

Table 1. Composition of Solutions Used to Electrodeposit Single Component Metals on Mo coated Si Substrates.

Metal	Solution Components	Grams/liter	Solvent
Molybdenum	MoO_3 H_2SO_4	10 5	H_2O
Copper	$CuSO_4$ H_2SO_4	8 16	H_2O
Indium	$In_2(SO_4)_3$ H_2SO_4	17.5 4.5	H_2O
Selenium	H_2SeO_3 H_2SO_4	12 15	H_2O

Copper electrodeposited at a current density of about 8 mA/cm^2 is uniform, quite smooth and has good adhesion on Mo. However, In and Se deposits are more rugged, and adhere poor to Mo. The adhesion and uniformity of the In and Se layers has improved significantly when a thin Cu film was first plated on Mo.

Codeposition of Cu-In-Se on Cu/Mo/Si was attempted using a mixture of the plating solutions for Cu, In and Se in Table 1, in (1:1:1) ratio. The CIS films had good adhesion to the Cu/Mo/Si substrate. Using qualitative EDAX spectra of Cu-In-Se films deposited at current densities of 5 and 8 mA/cm^2, we could not find significant differences, as expected, between the relative peak intensities of Cu, In and Se.

A well-known approach to improve the performance of CIS-based solar cells is to replace some of the In with Ga. By doing this the bandgap can be increased so as to obtain a better match to the sunlight spectrum. No Ga electrodeposition was attempted so far. In general, it is difficult to deposit simultaneously In and Ga ions from aqueous solutions containing In and Ga ions because of their different deposition potentials. However, is known that the deposition potentials of In and Ga ions from a non-aqueous solution of various halides are nearly equal, enabling the simultaneous deposition of In and Ga. The slight difference in their deposition potentials allows control of the In to Ga ratio in the deposit. A higher plating voltage should increase the proportion of Ga in the deposit and therefore the bandgap.

A possible combination of halides are indium trichloride and ammonium trichlorogallate, with ethylene glycol as a solvent. Since based on our first experiments, ammonium chloride does not appear to deposit on Mo or Cu, it can be used to increase the conductivity of the solution and, at the same time, to act as a flux. However, by using non-aqueous solutions are used for depositing In and Ga components, for the two other components of the CIGS layer, namely the Cu and Se, non-aqueous solution components should be used as well.

Chemical Bath Deposited CdS Films

As an aqueous solution method, the chemical bath deposited CdS films [7] presents many advantages, including: low-cost, low deposition temperature ($<90^oC$), relatively safe to use and large-area deposition. Using 2M ammonia (NH_4OH), 5 mM cadmium acetate dehydrate $\{Cd(CH_3COOH)_2 \ . \ 2H_2O\}$ and 0.2M thiourea $\{CS(NH_3)_2\}$, in proportions of (1:1:1) we were able to grow 30 to 60 nm (4 to 10 minutes growth time) of CdS films initially on Si substrates, and then on CIS layers grown by electrodeposition. The growth temperature was from 50^oC to 90^oC. Using mirror-like Si surfaces, the best morphology of the CdS surface films was obtained when a deposition temperature of 60 to 70^oC was used.

Conclusions

There is now growing interest in exploring the possibility of using thin film non-crystalline material, (e.g. $CuInSe_2$ polycrystalline thin film, amorphous Si, etc.) solar cells in space. Such cells, if they can be made to have beginning-of-life (BOL) 1 AMO, 25°C efficiency exceeding about 15%, have several advantages over the cells made from crystalline materials:

1) The thin film solar cells are comparatively very light weight and can be deposited on large plastic sheets or rolls. Such very light weight, large area rolls of solar cells are easy to stow during launch and recovery of the space satellite and also easy to deploy after launch of the satellite in space.

2) The thin film solar cells are comparatively much less expensive on the basis of dollars/peak watt.

3) In laboratory radiation damage experiments, both the a-Si and $CuInSe_2$ solar cells have shown a very high degree of radiation tolerance to 1MeV electrons and protons of various energies in comparison to crystalline semiconductor solar cells. Thus, if these noncrystalline material solar cells have the same high radiation tolerance in space as they do in the laboratory, a space satellite powered by these solar cells would have a much longer useful life in a high radiation environment such as the geosynchronous earth orbit (GEO).

Electrodeposition is potentially a low cost, high throughput method for the large scale manufacture of solar cells and solar electric panels because it is a well developed commonly used industrial process with a high yield.

Our proposed cell structure is: molybdenum/cooper (back contact) coated glass or kapton substrates/p-$CuIn_xGa_{1-x}Se_2$(CIGS)/n-CdS(buffer layer)/ n-ZnO (window layer)/MgF_2 (AR coating) with Ni-Al front grids.

In our approach, the main requirements of an effective thin film polycrystalline solar cell, namely: large area processing, low cost, and high material yield are assured since:

- all active layers of the cell: p-$CuIn_xGa_{1-x}Se_2$(absorber layer)/n-CdS(buffer layer)/n-ZnO(window layer) are deposited using low temperature wet chemical or electrochemical methods, which insures large area processing and low cost of the cell. If the silica or kapton substrates are coated with a thin conductive layer, electroplated Cu/Mo back contacts can be a good option for further reducing the cost.
- using known in-situ purification techniques (e.g. membranes), technical grade instead of semiconductor grade precursors can be used. These purification techniques can also be used for recycling used solutions (e.g. for separation of In and Ga), which ensures high material yield.

Additionally, from the point of view of safety, in comparison to other thin film deposition techniques, electrodeposition has the major advantage of containing the component elements of the film in aqueous solutions; this makes for easy containment and safe handling and disposal.

Requirements for low cost, high specific power solar cell arrays for space applications such as Lunar or Mars base might become even more demanding in the near future. Polycrystalline thin film solar cell technology offer the best hope for obtaining PV devices with low price and reasonable efficiency, stability and radiation resistance. For terrestrial, as well as for space applications the most promising thin film heterojunction cell structure for achieving the DOE efficiency goal set for these modules of 15% is $CdS/CuIn_xGa_{1-x}Se_2$ (CIGS). Cells based on electrodeposited CIGS absorber and solution grown CdS buffer layer show a very good chance for reaching this goal.

REFERENCES

[1] L. Stolt, J. Hedstrom, J. Kessler, M. Ruckh, K.-O. Velthaus and H.-W. Schock, Appl. Phys. Lett. 62, 597 (1993).

[2] J.Hedström, H. Ohlsén, M.Bodegård, A.Kylner, L.Stolt, D.Hariskos, M.Ruckh and H.-W.Schock, "ZnO/CdS/Cu(In,Ga)Se_2 Thin Film Solar Cells with Improved Performance," 23rd IEEE PVSC, 1993, pp. 364-371.

[3] W. E. Devaney, W. S. Chen, J. M. Stewart and R. A. Mickelsen, IEE Trans. Eletr. Dev. 37, 428 (1990).

[4] A. M. Gabor, J. R. Tuttle, D.S. Albin, M.A. Contreras and R. Noufi, Appl. Phys. Lett. 65, 198 (1994).

[5] C.Ferekides, J.Britt, Y.Ma and L.Killian, "High Efficiency CdTe Solar Cells by Close Spaced Sublimation," 23rd IEEE PVSC, 1993, pp. 389-393.

[6] H. Dittrich, T. Waqlter and H. -W. Schock, Proc. 10-th E.C. Photovoltaic Solar Energy Conf., Lisbon 1991 (Kluwer Academic Publishers, Dordrecht (1991) p. 917.

[7] T.L.Chu, S.S.Chu, C.Ferekides, C.Q.Wu, J.Britt and C.Wang, "High Efficiency CdS/CdTe Solar Cells From Solution-Grown CdS Films," 22nd IEEE PVSC, 1991, pp.952-956.

[8] G.C.Morris and S.K.Das, "Influence of $CdCl_2$ Treatment of CdS on the Properties of Electrodeposited CdS/CdTe Thin Film Solar Cells," 23rd IEEE PVSC, 1993, pp. 469-474.

[9] Y.Tyan and E.A.Perez-Albuerne, "Efficient Thin Film CdS/CdTe Solar Cells", 16th IEEE PVSC, 1982, pp. 794-800.

[10] K.W.Mitchell. C.Eberspacher, F.Cohen, J.Avery, G.Duran, and W.Bottenberg, "Progress Towards High Efficiency Thin Film CdTe Solar Cells," 18th IEEE PVSC, 1995, pp. 1360-1364.

[11] P.V.Meyers, "Design of a Thin Film CdTe Solar Cell," Solar Cells, 23, 59-67 (1988).

[12] J.F.Jordan and S.P.Albright, "Large Area CdS/CdTe Photovoltaic Cells," Solar Cells, 23, 107-113 (1988).

[13] A.K.Turner, et al., "Stable, High Efficiency Thin Film Solar Cells Produced by Electrodeposition of Cadmium Teluride," Technical Digest of the Int'l PVSEC-5, Kyoto, Japan, 1990, pp.761-764.

[14] S.Ikegami and A.Nakano, "Effect of Oxygen on Photovoltaic Properties of Screen Printed CdS/CdTe Solar Cell and Module," Int. J. Solar Energy, 12, 53-65 (1992).

[15] D.Bonnet, "The CdTe Thin Film Solar Cell - An Overview," Int. J. Solar Energy, 12, 1-14 (1992).

[16] K.Zweibel, "Toward Low Cost CdTe PV," Int. J. Solar Energy, 12, 285-292 (1992).

[17] P.V.Meyers, "High Temperature Vapor Deposition of Thin Film CdTe PV Modules," 11th PV AR&D Review Meeting, AIP Conference Proceedings 268, 1992, pp.250-254.

[18] J.Britt and C.Ferekidees, "Recent Advances in CdTe Solar Cells by Close-Spaced Sublimation (CSS)," Proc. 11th European PVSEC, 1992, pp.276-279.

[19] J.R.Sites, "Separation of Voltage Loss Mechanisms in Polycrystalline Solar Cells," 20th IEEE PVSC, 1988, pp. 1604-1607.

[20] J.M.Woodcock, A.M.Turner, M.E.Ozsan and J.G.Summers, "Thin Film Solar Cells Based on Electrodeposited CdTe," 22nd IEEE PVSC, 1991, pp.842-847.

[21] G.C.Morris and S.K.Das, Int. J. Solar Energy, 12, 95 (1992).

[22] D.Haritos, M.Ruckh, U. Ruhle, T. Walter, and H.W. Schock, "A Novel Cadmium Free Buffer Layer for $Cu(In,Ga)Se_2$ Based Solar Cells," 1st WCPEC, Dec. 5-9, 1994, Hawaii, p.91.

[23] D. Lincot, et al. "Tailoring the electronic properties of one step electrodeposited $CuInSe_2$ films by annealing in Se vapor under controlled activity conditions. Elaboration of efficient CIS/ZnO solar cells," 1st WCPEC, Dec.5-9, 1994, Hawaii, p.136.

[24] M.P.R. Panicker, M. Knaster and F.A. Kroger, J.Electrochem. Soc. 125, 566 (1978).