Preparation and Characterization of Spray Deposited CuO thin Films towards Fabrication of Low Cost Hetero-junction Solar Cells

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ABSTRACT

Copper oxide (CuO) thin films of various thicknesses (125-300 nm) were deposited in a multi-cycle on Si (100) substrates at a temperature of 350 ^{o}C by Spray Pyrolysis technique under optimum conditions, for application as the absorber layer for hetero-junction solar cells. The structural, morphological and compositional studies of the films were made through XRD, SEM and EDAX techniques. XRD studies reveal that the films are crystalline and much less strained. The average grain size of the films, as estimated from SEM studies, was 12.28 nm. The resistivity of films was optimized by performing isochronal and isothermal studies on films, by annealing in air at different timings of 15-120 min and temperature in the range from 100 - 400 ^{o}C, respectively. Films found to possess resistivities in the range of 1.33×10^{-2} - 1.214×10^{-2} Ωcm. The capacitance as a function of frequency on the junction confirms the existence of large interface states of 5.752×10^{10} $Fcm^{-2}eV^{-1}$ due to plenty of pin-holes inside the sprayed films. The estimated values of barrier height, ideality factor and reverse saturation current from M-S-M studies were found to be 0.767 eV, 0.7936 and 2.832×10^{-9} A, respectively. The influence of thickness of CuO films on Au/CuO/nSi/Al hetero-junction solar cells characteristics were made and the estimated cell parameters such as series resistance, shunt resistance, open circuit voltage, short circuit current, fill factor and efficiency were found to be in the range of 0.333–32.46 kΩ, 9.01–860 kΩ, 200–325 mV, 21– 72 μA, 17-24 % and 3.46×10^{-3}-9.71×10^{-3} %, respectively.

Keywords: CuO; Isothermal; Spray pyrolysis; thickness; solar cell

1. INTRODUCTION

Copper (II) oxide (CuO) is a semi-conductor with p-type conductivity [1]. The direct optical band gap energy values of 1.3-2.1 eV [2, 3] have been reported for CuO. The two basic requirements for materials to be used as solar cell windows are a high optical transmittance in the visible wavelength range and low electrical resistivity. CuO absorbs strongly throughout the visible spectrum and is black in appearance [4]. The electrical transport properties of thin films are strongly dependent on their structure such as grain size, defects and or purity, namely nature and concentration of impurities. Heat treatment of thin films affects the structural characteristics and hence the conductivity of such films may change too [5]. The current potential application areas of copper oxide thin films include solar cells and electro-chromic devices [1, 4]. Copper oxide films have been reported to have band gap energy values, which make them suitable for application as windows for solar energy conversion [1, 6]. Richardson [7] has also highlighted the potential of copper oxide films as spectrally selective variable reflectance coatings for radiant energy control in architectural and aerospace applications.

Photovoltaic device which converts solar light into electrical energy is most suitable for the production of convenient and low cost energy. But major problem here is the development of easily available and eco friendly absorbers that can give reasonably high efficiency cells. Although single crystal Si solar cells already have efficiency over 15 % which is very close to the theoretical value, the high cost of Si solar cells becomes the most vital obstacle to commercialize. Finding cheaper material and a simple process becomes the effective way to reduce the cost. Therefore, the low-cost solar cells have gained more attention recently. One of the good candidates is hetero junction solar cells formed simply by depositing transparent semiconductor films such as CuO on Si substrates. The hetero junction solar cells have a number of potential advantages such as an excellent blue response, simple processing steps and low processing temperatures [8]. Relatively high conversion efficiency in 12-15 % range has been obtained by employing spray-deposited ITO films on Si substrates [9]. CuO films are preferred over ITO due to lower cost and abundant resource of copper on the earth. Several techniques have been used for the preparation of CuO thin films, which include sputtering [10], chemical vapor deposition [11], molecular beam epitaxy [12] and spray pyrolysis [13]. Probably, the spray pyrolysis is the cheapest and elegant technique towards preparation of thin films. In this view, study of CuO films with moderate band gap, good electrical and optical properties, less toxicity, low cost and lower deposition temperature, is chosen as a potential candidate for solar cell applications [14]. The films prepared by Spray pyrolysis are of better crystalline quality, clean, adherent, having higher density and lower porosity etc., which are favorable characters for solar cell and sensors [14, 15]. It needs no vacuum because the films are deposited in the atmospheric ambiance. Many works [16, 17] pay attention to heavily doped CuO for its potential use as solar cell absorber. CuO [18] can be used not only as solar cells absorber layer but also as hetero-junction partner. CuO /Si junction has a simple structure and an excellent photovoltaic (PV) device.

In the present investigation, intrinsic Copper oxide (CuO) film as an absorber layer was deposited by spray pyrolysis on n-type Si substrate to form a hetero-junction solar cell. The electrical characteristics of these solar cells were studied. The annealing studies on films towards optimization of resistivity as well as influence of absorber layer thickness on cell properties were reported.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation

Mirror-like single crystal n-type (100) Si wafer, with a thickness of 350 μm and a resistivity of 1-3 Ωcm, was used as a substrate in this study. Wafer cleaning is an important and critical step in device fabrication as any chemical contamination (metallic or organic) can ruin the device performance and reliability. RCA cleaning process was used for removing any particles or any chemical contaminations present on the wafer by using 2 sequential cleaning solutions, namely standard cleaning-1 (NH_3-H_2O_2-DI water in composition of 1:1:5 to remove native oxide present on the wafer) and standard cleaning-2 (HCl-H_20_2-DI water in composition of 1:1:6 to remove metal contamination on the wafer), respectively. The cleaning process was followed by a dilute HF dip and then washed with deionized water to passivate the Si dangling bonds with hydrogen. Copper Oxide (CuO) thin films of various thicknesses (125-300 nm) were prepared under optimum conditions [19] in multi cycle (3,7 cycles) by varying deposition time (15 s, 25 s) on cleaned silicon substrates at 300 ºC by spraying a 0.01 M of Cupric acetate ($(CH_3COO)_2$ CuH_20 ; Sigma Aldrich) dissolved in double distilled water.

Au contacts were made over CuO films, by coating desired metal over films through a mask with an area of 1.963 x 10^{-3} cm^2 using RF sputtering technique. Anelva SPF-332H make RF sputtering unit with deposition parameters such as target to substrate distance 5.2 cm, plate voltage 1-2 kV , plate current 60-110 mA , incident power 40-150 W, reflecting power 5-25 W. pre sputtering time 5-20 min and pressure of 6 m Torr was utilized. Aluminum films of thickness 150 nm are coated on back surface of each silicon substrate using thermal evaporation technique. Hindhivac 15F6 make thermal evaporation unit with deposition parameters such as vacuum pressure 0.0752 μ Torr, boat voltage and current 20-30 V and 50 A were utilized. Film thickness was investigated using DekTak3 Profilometer and was found to vary from 125-300 nm. Fig. 1 shows the cross section of CuO/n-Si solar cell. Hetero-junction solar cells were fabricated using the configuration Au/CuO/n-Si/Al.

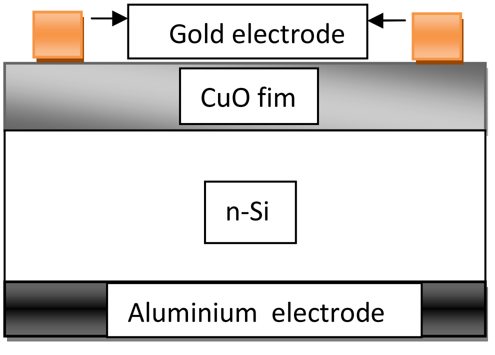


Fig.1. Cross-section of p-CuO/n-Si hetero-junction solar cell

2.2 Sample characterization

The crystal structure of grown films was investigated using an X-ray diffraction (XRD) with Cu-K_α source. The power output of the solar cell was measured using Agilent 4155C semiconductor parametric analyzer under AM1 condition. The SUSS PMS Analytical Prober was used for device probing, since probe shield protects the device from electromagnetic and radio frequency interference. Tungsten probe tips were used for probing devices.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD pattern of as deposited CuO thin films prepared by spray pyrolysis at a substrate temperature of 300 $^\circ$C is shown in Fig.2. The CuO films possess monoclinic structure and show reflections along ($\bar{1}$11), (111), (120) and (013) at 2θ = 35.392°, 38.99°, 58.31° and 62.19°, respectively [20].

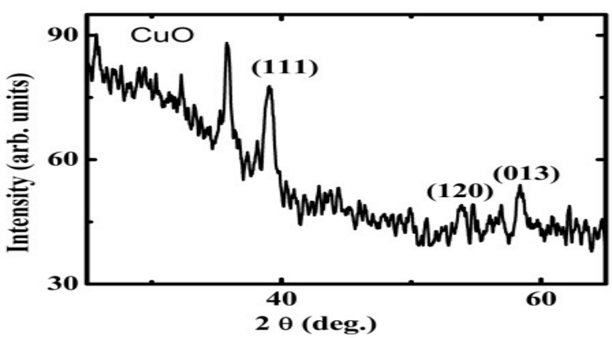


Fig.2. XRD patterns of spray pyrolized CuO thin films.

The average grain size (D_{AG}), microstrain (ε) and dislocation density (δ) were estimated [21, 22]. The average grain size was estimated using the Scherrer formula,

$$D_{AG} = \frac{0.94\,\lambda}{\omega \cos \theta}, \quad (1)$$

where λ is the wavelength of X-ray (1.54 Å) , θ is the Bragg angle and ω is the full width at half maximum (FWHM) of the XRD peaks. The microstrain (ε),

$$\varepsilon = \frac{\omega \cos \theta}{4}, \quad (2)$$

and the dislocation density (δ) defined as the length of dislocation lines per meter^3,

$$\delta = \frac{1}{D_{AG}^{2}} , \qquad (3)$$

estimated. The estimated values of average grain size (D_{AG}), microstrain (ε) and dislocation density (δ) of CuO films found to be 175 nm, 8.22×10^{-4} $lin^{-2}m^{-4}$ and 3.265×10^{13} lin m^{-2}. This shows that the films are crystalline and much less strained.

3.2. SEM analysis

The scanning electron micrographs (SEM) of as deposited CuO thin films produced by spray pyrolysis at a substrate temperature of 300°C are displayed in Fig.3. The grain size of the films as estimated from SEM studies was found to be 12.28 nm. The grain size as observed from SEM is different from the average grain size that is reported from XRD. Similar kind of discrepancies was reported by Korotcenkov et al. (2005) [23] for SnO_2 films prepared by spray pyrolysis. The grains being a collection of small crystals, TEM pictures may reveal the multi nature of the grains.

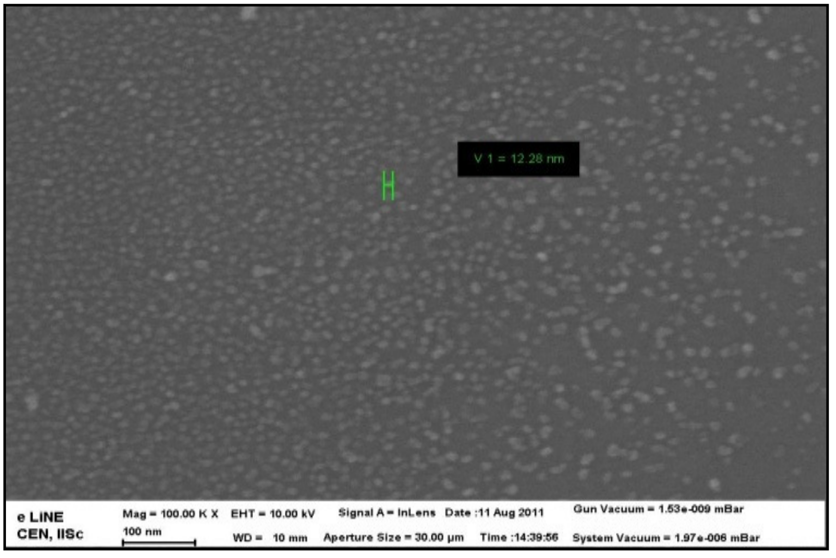


Fig.3. SEM micrographs of spray pyrolized CuO thin films.

3.3. EDAX analysis

The chemical composition of the as deposited CuO spray pyrolized thin films was determined by Energy Dispersive X-ray Analysis (EDAX). From EDAX analysis, it is found that the element weight % in CuO is (Cu -89.78 %, O-10.22 %), respectively. No other elemental impurities were detected in these films.

3.4. Isochronal and isothermal annealing studies

Isochronal annealing studies were made on as deposited CuO thin films prepared by spray pyrolysis technique on Si (100) substrates. The studies were made by annealing films in air at different temperatures ranging from 100 – 400ºC for a constant time of 30 min. The electrical resistivity of these samples was then measured by four point probe technique (Model 280). Plot of sheet resistivity ρ_s of thin films at ambient temperature (27ºC) as a function of annealing temperature is shown in fig. 4 (a). From the plot it is clear that the sheet resistivity of films found to vary between 1.33 x10^{-2} Ωcm - 1.216 x10^{-2} Ωcm with increase in annealing temperature from 27ºC to 400ºC. From the study it is also found that the sheet resistivities of films reach lowest resistivity of 1.214 x10^{-2} Ωcm at annealing temperature of 300^0 C. From the plot it is observed that in films there is rise and fall of sheet resistivity with increase in temperature. This type of behavior is normally observed for disordered materials. The rise in resistivity due to heat treatment in air may be associated with decrease in carrier density by filling up of oxygen vacancies and fall in resistivity may be attributed to rearrangement and removal of defects as well as improvement in the grain structure or crystallinity.

Isothermal studies were also made on CuO as deposited thin films by annealing at constant temperature of 300ºC in air for duration ranging from 15 - 120 min. Plot of sheet resistivity ρ_s of thin films at constant temperature and as a function of annealing time is shown in fig.4 (b). From the plot it is observed that the sheet resistivity reach lower value of 1.266 x10^{-2} Ωcm at 60 min (300ºC) for CuO films. The obtained films were of comparable quality of those deposited elsewhere for use as absorbing layers in solar cells.

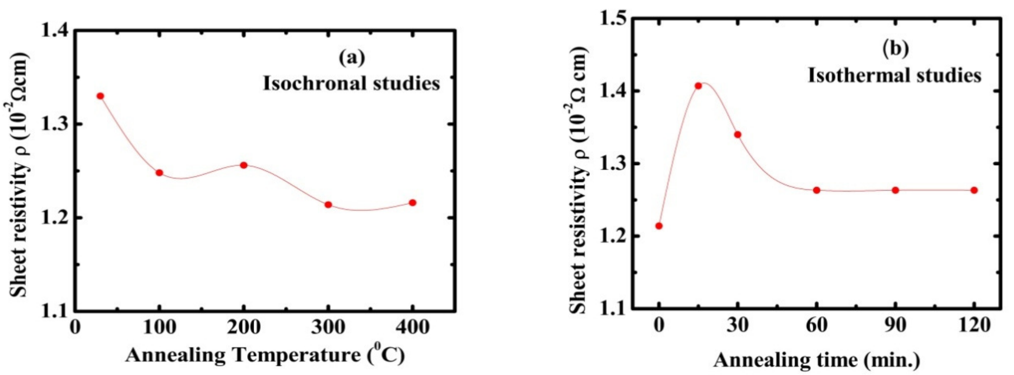


Fig.4. (a) Plot of sheet resistivity 'ρ_s' of CuO thin films as a function of annealing temperature.
(b) Plot of sheet resistivity 'ρ_s' of CuO thin films as a function of annealing time.

3.5. Metal-Semiconductor-Metal studies

Au-CuO-Au, MSM studies were made by probing on metal-metal contacts (inset Fig. 5) of Au/CuO/n-Si/Al configuration hetero-junction solar cells. The electrical characterization of these films was made using 4155C semiconductor parametric analyzer. The I-V curve of the devices is drawn in fig.5. From the I-V curve, it is observed that the current increase exponentially with increase in forward bias voltage. Under forward bias (I) current flowing across a rectifying metal-semiconductor contact in a p-n junction under bias V is usually modeled as

$$I = I_s\, e^{\left(\frac{qV}{nTk_B}\right)}, \qquad (4)$$

Where $\left(\frac{q}{Tk_B}\right)$ represents inverse thermal voltage, k_B is Boltzmann constant, n is ideality factor, T is absolute Temperature, I_s is reverse saturation current and q is electronic charge. The Saturation current I_s is usually described within the Thermionic emission theory of semiconductor as

$$I_s = A^* A\, T^2 e^{\left(\frac{-\phi_b}{Tk_B}\right)}, \qquad (5)$$

Where A* is the Richardson constant, A is the surface area of the diode and φ_b is the barrier height or potential. From the plot, the electrical parameters such as reverse saturation (dark) current, ideality factor and barrier potential were evaluated using the equations (4) and (5). Bhuvaneswari et.al. [24] have used theoretical formulae for estimation of electrical parameters for zirconium nitride films. The estimated values of reverse saturation current, ideality factor and barrier potential were found to be 2.832 $\times 10^{-9}$A, 0.7936 and 0.767 eV. Lower reverse saturation current may be due to higher barrier potential at the interface. Lower dark current may be due to the trapping of charge carriers inside the pinholes, which are in plenty inside sprayed films.

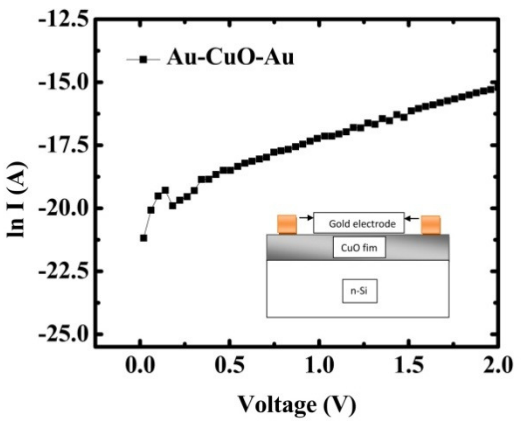


Fig.5. Plot of forward bias I-V curves

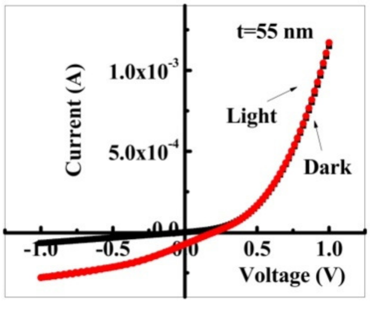
3.6. Solar cell performance

The cells having effective area of 0.176 cm^2 were illuminated with 150 W halogen lamp. The I-V characteristics were measured and plotted in fig. 6. The dark-light I-V characteristics of cells namely Au (150 nm, 150ºC)/CuO (125-300 nm)/n-Si/Al (150 nm,150ºC) have shown excellent rectifying behavior of hetero junction solar cells. Fig.7 shows the I-V characteristics of the hetero-junction solar cells under illumination of 206 mW/cm^2. For estimating interface states at the CuO/Si interface, capacitance as a function of frequency measurements was made. The values of capacitance namely, C_{LF} and C_{HF} were measured by 4155C semiconductor parametric analyzer. From these values of capacitance, number of interface states (N_{is}) was estimated. The total number of interface states due to depletion and interface can be calculated from the capacitance measured at low frequency while the capacitance at high frequency is associated with depletion only. A lower limit of interface states N_{is} can be calculated from the relation

$$N_{is} = \left(\frac{C_{LF}-C_{HF}}{e}\right), \qquad (6)$$

Where C_{LF} and C_{HF} are the capacitance at low (50 Hz) and high (1kHz) frequencies, respectively [25]. The estimated values of C_{LF}, C_{HF} and N_{is} were found to be 7.43 nF, 5.81 nF and 5.752×10^{10} $Fcm^{-2}eV^{-1}$, respectively. Large number of interface states at the interface confirms the existence of pin-holes which are in plenty inside the sprayed CuO thin films.

The diode parameters using fig. 6 are shown in Table-1. The diode (ideality) factor ‘n’ of the junction was found to vary from 0.194-0.973, confirming that interface recombination is the dominant mechanism in these junctions. With illumination of light on the junction, it is observed that the ‘I_S’ decrease as a result of increase in ‘n’ as well as ‘$\square_b$’. With the increase in thickness of CuO films, similar kind of changes in diode parameters are observed. However some of the diode parameters are inconsistent.



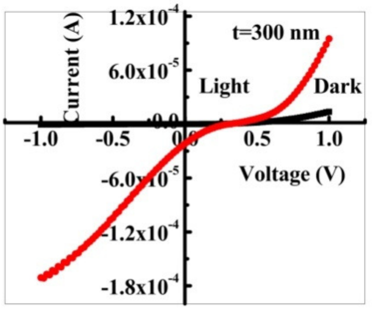


Fig.6. Dark- light I-V characteristics showing rectifying behavior of Au/CuO/n-Si/Al hetero-junction solar cells.

Table 1 : Cell parameters under dark and light conditions

Hetero-junction solar cell	$I_{0(Dark)}$ µA	Barrier Potential $Ø_{b\ (Dark)}$ eV	Ideality factor $n_{(Dark)}$	$I_{0(Light)}$ µA	Barrier Potential $Ø_{b\ (light)}$ eV	Ideality factor $n_{(Light)}$
CuO (125nm)/n-Si	32.24	0.525	0.194	26.63	0.530	0.536
CuO (300nm)/n-Si	0.428	0.637	0.264	1.083	0.613	0.973

The estimated cell parameters using fig.7 are shown in Table-2. In general the cells have high series resistance, high shunt resistance, low short circuit currents (i_{sc}), low open circuit voltages (V_{OC}), small Fill Factors (FF) and consequently low efficiencies (eff). On illumination, it is observed that the series as well as shunt resistance increase due to decrease in dark current. Higher series resistance may be due to the total sum of resistances at the n-Si/p-CuO junction, Au - CuO contact and Au as well as Al metal contacts. The shunt resistance is high, due perhaps to the recombination along the grains and the defects which are in large number in sprayed films. With the increase in thickness of CuO films, the cell parameters such as FF, eff and i_{sc} found to decrease. This may be due to the increment in V_{OC} as well as series resistance at the junction. The heat treatment process of the CuO film coated on Si substrate seriously influences the photovoltaic properties due to the change of the surface state of Si substrate by oxidation and contamination. This may be one of the reasons for the inconsistency [26] in the photovoltaic properties of hetero-junction solar cells.

Table 2. Performance results of solar cells prepared by spray-deposition.

Hetero-junction solar cell	R_{eries} (Dark) kΩ	R_{Series} (Light) kΩ	R_{Shunt} (Dark) kΩ	R_{Shunt} (Light) kΩ	V_m mV	i_m µA	V_{oc} mV	i_{sc} µA	FF %	Eff 10^{-3} %
CuO(125nm)/n-Si	**0.333**	**0.333**	**14.92**	**9.01**	**100**	**35.0**	**200**	**72.9**	**24.0**	**9.71**
CuO(300nm)/n-Si	**32.46**	**3.16**	**860**	**40.8**	**125**	**9.99**	**325**	**21.7**	**17.7**	**3.46**

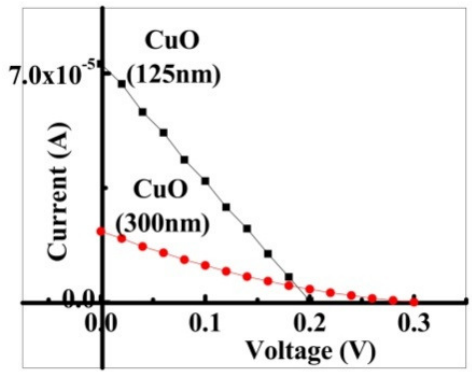


Fig.7. I-V characteristic of the hetero-junction solar cells with active area of (0.175 cm^{-2}) under 206 $mWcm^{-2}$ illumination.

4. CONCLUSION

Copper oxide (CuO) thin films of various thicknesses (125-300 nm) were successfully deposited in a multi-cycle on Si (100) substrates at a temperature of 350 $^{\circ}C$ by spray pyrolysis technique under optimum conditions, for application as the absorber layer for hetero-junction solar cells.. The structural, morphological and compositional studies of these films were made by analyzing XRD, SEM and EDAX. XRD studies reveal that the films are crystalline and much less strained. The resistivity of films was optimized by performing isochronal and isothermal studies on films by annealing in air at various temperature and timings, respectively. The capacitance as a function of frequency on the junction confirms the existence of large interface states at the interface. The M-S-M study shows the decrement in dark current due to higher barrier at the interface. The current-voltage studies of cells in dark and under illumination shows excellent rectifying behavior of hetero-junctions. The influence of increase in thickness of CuO films on Au/CuO/nSi/Al hetero-junction solar cells were made and the estimated cell parameters such as series resistance, shunt resistance, open circuit voltage, short circuit current, fill factor and efficiency were found to be in the range of 0.333 – 32.46 kΩ, 9.01 – 860 kΩ, 200 – 325 mV, 21 – 72 μA , 17 - 24 % and 3.46×10^{-3} -9.71×10^{-3} %, respectively. Better cell parameters may be further obtained by improving the quality of sprayed films, decreasing deposition cycles, varying absorber thickness, reducing the resistivity of films either by annealing in air or vacuum, doping and also by adjusting spray parameters.

5. ACKNOWLEDGEMENTS

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