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Optimization of the growth conditions of Cu_2O thin films and subsequent fabrication of Cu_2O/ZnO heterojunction by m-SILAR method

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***Abstract*— Cuprous oxide (Cu_2O) and zinc oxide (ZnO) thin films are the most preferable p-type and n-type materials respectively for preparing all oxide based solar cells. In this study, both Cu_2O and ZnO thin films were prepared by modified Successive Ionic Layer Adsorption and Reaction (m-SILAR) method. During the growth of Cu_2O phase, the pH conditions were optimized at 7.95 and 5.20 which were then annealed at 350 ℃ for 1 hour. Both XRD and Raman of unannealed and annealed samples showed peaks for Cu_2O and CuO films, respectively. The estimated band gap was in the range 2.07-2.16 eV for Cu_2O and 1.43-1.51 eV for CuO thin films. For Cu_2O phase, the activation energy was found in the range of 0.004~0.19 and 0.01~0.68 eV at the temperature range 40-90 ℃ and 100-250 ℃, respectively. Finally, diode like I-V characteristic behavior was observed for the m-SILAR grown Cu_2O/ZnO heterojunction.**

Keywords—m-SILAR, Cu_2O, ZnO, activation energy, band gap, diode

I. INTRODUCTION

Metal oxides are the most prominently used semiconductor in thin film solar cell preparation because of their abundance on earth crust and their nontoxic nature which leads to the cost effective and environment friendly photovoltaic cells [1, 2]. Though copper oxide can exist in two different stable forms (cubic Cu_2O and monoclinic CuO), Cu_2O is the most promising p-type absorber material because of its direct band gap nature (Eg ~ 2.17 eV), higher mobility and a very good alignment of band gap with n-type counterpart ZnO (Eg ~ 3.37 eV). The ZnO has been chosen as n-type material because it also has the direct band gap nature and high transmittance in the visible region as well as its low and adjustable electrical resistivity [3, 4]. Among the different methods of thin film solar cell preparation, SILAR is rapid, easier, economically favorable which produces large area thin films [5, 6] literally in any kind of substrates.

In our prior study, the SILAR method has been adopted by excluding the two rinsing steps and named as modified SILAR (m-SILAR) method [7]. In this report, the pH level of precursor solution for Cu_2O thin film preparation was optimized at 5.20 and 7.95 while immersion cycle was fixed at 60 and the annealing temperature was set to 350 ℃ for 1 hour in air.

II. EXPERIMENTAL SECTION

Cu_2O and ZnO thin films were deposited on both soda lime glass (SLG) microscope slides and Fluorine- doped Tin Oxide (FTO) substrates by m-SILAR method using a complex mixture of 1M $CuSO_4$ and 1M $Na_2S_2O_3$ (1:4) solutions. The pH of this cationic precursor was maintained at 7.95 and 5.20 by adding acetic acid solution systematically. Then the substrates were immersed alternatively first in a hot solution (2M NaOH at 70 ℃) and then in the cold precursor solution for 5 seconds. Samples grown on FTO substrates were annealed at 350 ℃ for 1 hour. The heating rate was 5 ℃/minute. Then ZnO thin films were deposited on the annealed sample by using zinc ammonia complex solution and hot isopropyl alcohol. These samples were again annealed at 200 ℃ for 1hour [8]. The thickness of the samples was measured by a simple gravimetric method [5]. The optical, electrical, photovoltaic properties, crystalline structure and Raman spectra were characterized by using UV-VIS-NIR spectrometer (λ = 220-1400 nm) coupled with an integrating sphere (Shimadzu 2600 ISR plus), a home made four-point collinear probe setup, a homemade multi probe working station coupled with a Keithley 2450 SMU (IPD, BCSIR), X-ray Diffraction Spectroscopy with CuKα (λ = 0.15406 nm) radiation source (Philips PANalytical X'Pert MRD) and Raman Spectroscopy (Horiba HR800) with 488 nm laser excitation energy. Moreover, the temperature dependent surface resistivity was measured in the ranges 40-90 ℃ and 100-250 ℃ respectively to estimate the activation energy.

III. RESULTS AND DISCUSSION

A. Optimization of the Properties of Cu_2O Thin Films

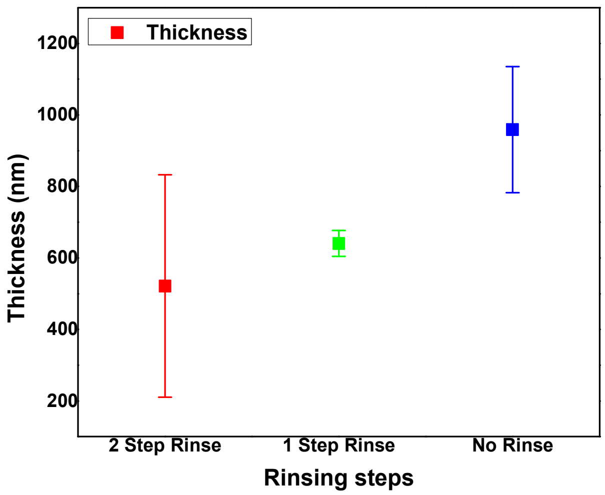

Fig. 1. Variation of film thicknesses with rinsing steps.

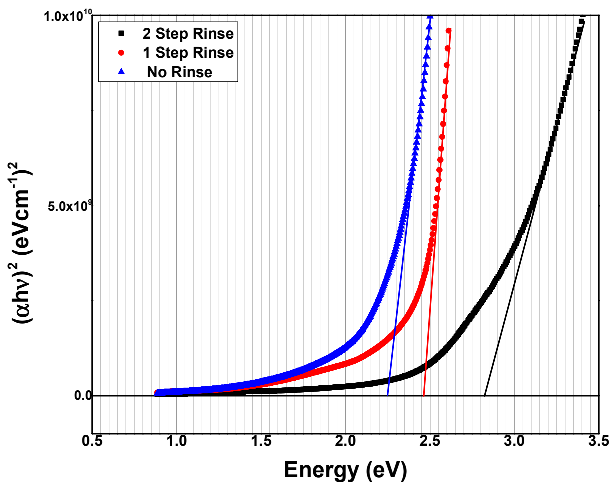

Fig. 2. Variation of band gap with rinsing steps.

Figs. 1 and 2 show the variation of thicknesses and band energies with rinsing steps. It is evident that by excluding the rinsing steps the thickness of the thin Cu_2O films increases while the band gap decreases. Due to the rinsing steps films are etched and destroy the quality of films. So, we excluded these steps and adopted it as m-SILAR method.

Fig. 3 shows the XRD pattern of m-SILAR grown cuprous oxide thin films at pH range ~4.50-7.95 for 60 cycles. It is evident here that Cu_2O phase is polycrystalline in nature and dominated by strong Bragg's peak arising from (111) at 2θ ≈ 36.5° which are in close agreement with our previously reported works [5]. The X-ray diffractograms also reveal that there is an increasing trend of (111) texturing in the m-SILAR grown cuprous oxide thin film with increasing solution pH. The mixture of Cu_2O and CuO phases have been observed [7] for annealed (350 ℃ for 1 hour) samples on FTO substrate. This observation implies that the Cu_2O phase is not completely converted to CuO upon 1-hour annealing [7].

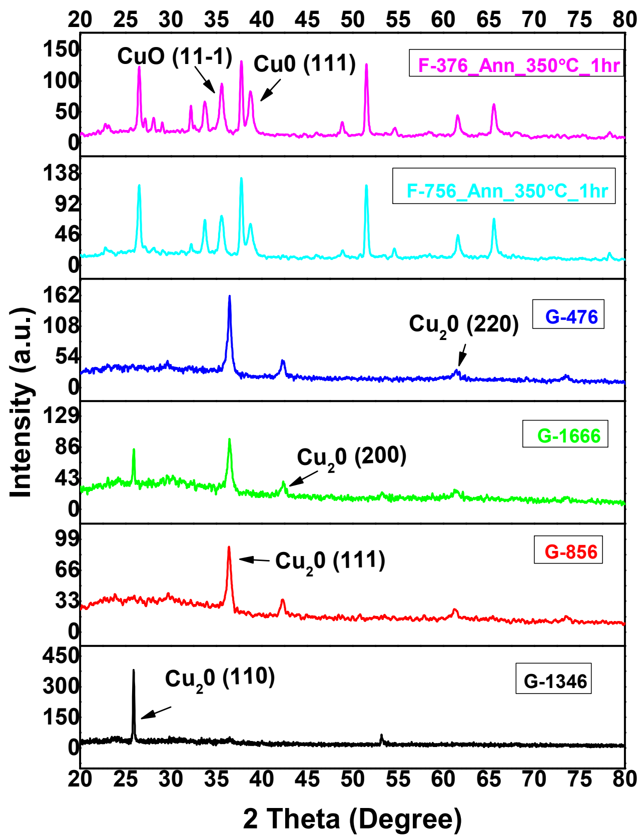

Fig. 3. XRD patterns of samples grown on glass and FTO substrates at different pH for 60 cycles.

Fig. 4 shows Raman spectra for as prepared and annealed samples grown at different pH's. The spectrum of G-1346, G-856, and G-1666 exhibit peaks at 150, 220, 400 and 635 cm^{-1}. Analogous bands were observed in previously reported works for Cu_2O phases [3,9]. The annealed samples grown on FTO substrates showed Raman peaks at 125, 296, 340 and 635 cm^{-1} which correspond to CuO bands [10].

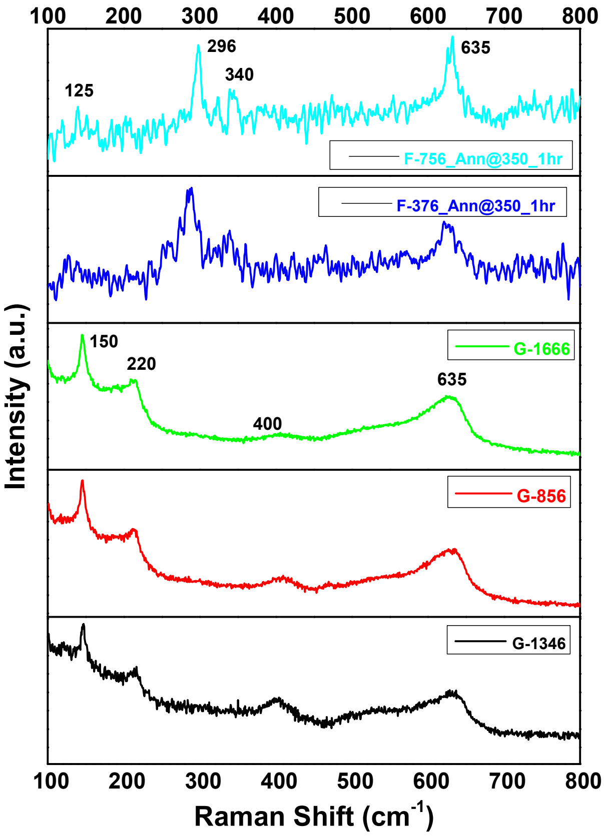

Fig. 4. Raman spectra of samples grown on glass and FTO substrates at different pH for 60 cycles.

The temperature dependent surface resistivity was measured in the temperature range of 40- 250 ℃ and the respected activation energy values are tabulated in Table I. From the table, it is evident that the activation energy was in the range of 0.004~ 0.19 and 0.01~ 0.68 eV at the temperature range 40- 90 ℃ and 100-250 ℃, respectively at various pH grown Cu_2O thin films. The reported value of activation energy is 0.20- 0.24 eV for Cu_2O [11].

TABLE I. ACTIVATION ENERGY OF DIFFERENT SAMPLES AT TWO TEMPERATURE RANGES

Sample ID	pH	Activation energy (eV)	
		40-90 ℃	100-250 ℃
G-1346	4.50	0.190	0.680
G-856	5.20	0.087	0.012
G-1666	6.20	0.004	0.102
G-476	7.95	0.078	0.035

B. Fabrication of p-n Junction and Analysis

Both the figures (Figs. 5 and 6) show a diode character of the FTO/Cu_2O/ZnO p-n heterojunction and would allow current to flow in one direction while utilized Cu_2O layer optimized at pH of 7.95 and 5.20, respectively. From Fig. 5, we observed I-V characteristic curve under dark and white LED illumination. An apparent breakdown voltage at almost -0.5 V at which the diode become conductive to negative current. Intriguingly, the ZnO/Cu_2O (F-176) was found to be more conducting with the increasing of LED intensity contrary to the solar cell behaviour. The full intensity (FI = 100%) of white LED when measured by a solar power-meter (TES-1333) was produced optical power (P) of ~45 mW/cm^2 and half intensity (HI=50%) of LED produced P of ~ 12 mW/cm^2. In case of the ZnO/Cu_2O (F-556) junction (see Fig. 6), FI produced a downward shifting of I-V but no discernible solar cell behaviour. Further experimental investigations are needed to optimize the cell structure to use these m-SILAR grown metal oxides for photovoltaic application.

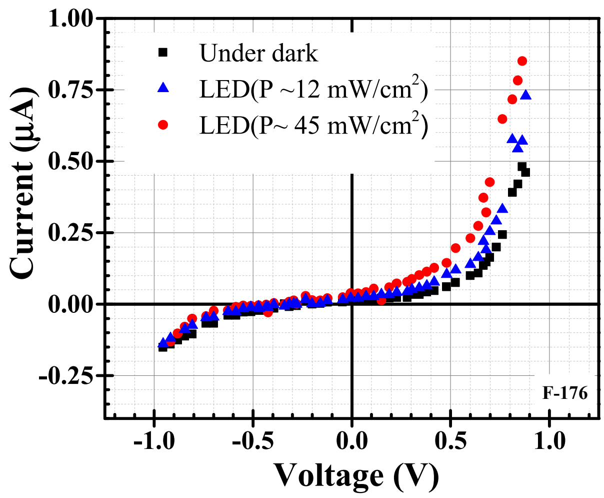

Fig. 5. I-V characteristic curve for FTO/Cu_2O/ZnO heterojunction cell grown on FTO substrate at pH- 7.95.

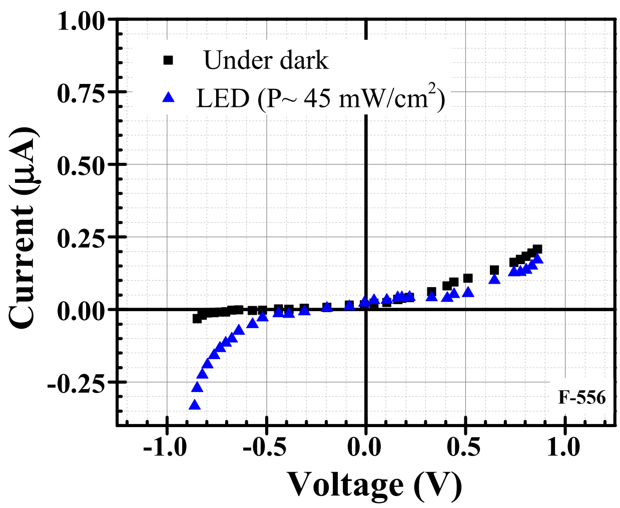

Fig. 6. I-V curve for FTO/Cu_2O/ZnO junction cell grown on FTO substrate at pH- 5.20.

IV. CONCLUSION

A comprehensive study of the optimization of properties of Cu_2O thin films prepared by m-SILAR method and the characteristic diode like behavior of FTO/Cu_2O/ZnO p-n heterojunction is presented in this work. Optimization of the growth conditions of Cu_2O thin films were examined with respect to pH as well as rinsing steps during film fabrication for 60 cycles. Physical properties of copper oxide thin films were characterized by UV-VIS- NIR, XRD, Raman and electrical properties like resistivity results were reported. The activation energies for Cu_2O thin films were also studied at different temperature regions. We have been continuing our p-n heterojunction cell preparation and characterization at this two pH's. A preliminary study of solid FTO/Cu_2O/ZnO junctions revealed diode like I-V curves. Further experimental investigations are currently in progress to optimize the cell structure for working as a solar cell.

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