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INVESTIGATION OF n-Cu_2O QUANTUM DOTS ON A p-Cu_2O THIN FILM

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ABSTRACT

This research consists of two steps. In the first step p-type Cu_2O nano-surface is obtained using thermal oxidation method, in the second step prepared p-type Cu_2O samples were quenched in a 0.1 M $CuSO_4$ solution and investigated for presence of n-type Cu_2O quantum dots on the p-type Cu_2O thin film. p-type Cu_2O thin films were fabricated using two thermal oxidation methods. In 1st method p-type Cu_2O nano-surfaces were fabricated by heating of well cleaned Cu plates (98.9% purity) up to 300°C for 30min maintaining a heating rate of 100°C/min. In 2nd method well cleaned Cu plates (98.9% purity) were kept in oven chamber for less than 2min, while keeping oven chamber temperature in 900°C. Sample was characterized with diffuse reflectance measurements and calculated direct band gap of p-type Cu_2O was 1.96eV. After the verification of p-type Cu_2O nano-surface, quenching in 0.1 M CuSO4 solution was carried out for p-Cu_2O thin film samples fabricated by both methods. After quenching samples were kept in the $CuSO_4$ solution for time periods 48, 24, 12 and 6 hours. Diffuse reflectance spectrum and VI characteristics of quenched samples were taken and results were investigated for formation of n-type Cu_2O quantum dots on p-type Cu_2O thin film.

Keywords: p-type Cu_2O, n-type Cu_2O, Quantum dots, Thermal oxidation, Quenching

1. INTRODUCTION

Technology and material used in photovoltaic devices are changing from time to time over the past decade till now, as the need for clean and renewable energy rises. With the advancement of technology industry has a tendency to explore new ways to fabricate low-cost material for solar energy conversion devices. Bulk semiconductor solar cell, dye sensitized solar cell materials were fabricated and quantum dot sensitized solar cells are emerging in the industry to meet the requirement. Quantum dots are semiconductor

nanocrystals which contains a small finite number (of the order of 1-100) of conduction band electrons, valence band holes, or excitons[2]. Unlike traditional semiconductors which have limitations, where their optical and electronic properties are not easily adjustable as their band gaps are not easily changeable. But Quantum Dot (QD) band gaps can be changed by changing their size[3]. Electronics properties QDs display unique electronic properties intermediate between electronic properties of bulk semiconductor and discrete molecules. QDs confines the motion of conduction band electrons, valence band holes or bound pairs of conduction band electrons and valence band holes (excitons) in all three spatial directions[4]. QDs are capable of Multiple Exciton Generation (MEG) or Multiple Carrier Generation, where single photon creates more than one exciton[5].

This study discusses a method to fabricate n-type Cu_2O quantum dots on a p-type Cu_2O thin film. Thermal oxidation method was used in fabricating p-type Cu_2O, while quenching method was used in fabricating n-type Cu_2O quantum dots on p-type Cu_2O film. Cu_2O is naturally p-type conducting semiconductor material with "Reddish Brown" color and has direct band gap energy of 2.1 eV[1].

2. EXPERIMENTAL

2.1 p-Cu_2O preparation with thermal oxidation:

Method 1: A 25mm x 15mm Cu plate (98.9% purity) was well cleaned using sand paper, detergent and distilled water to remove oxide layer, oil and dust. Cleaned Cu plate was placed in the furnace (Carbolite ELF11) and heated with 100°C/min heating rate until furnace chamber temperature goes to 300°C. Sample was kept in 300°C for 30min to grow p-Cu_2O on top of the Cu substrate; temperature profile shown in Figure 1 was followed.

Method 2: Oven chamber temperature was set to 900°C with 100°C/min heating rate. After oven chamber has risen to 900°C, well cleaned 25mm x 15mm Cu plates (98.9% purity) were placed in the oven for very short time periods(less than 2min) to grow p-Cu_2O on top of the Cu substrate.

2.2 Fabrication of n-Cu_2O quantum dots on p-Cu_2O thin film by quenching method:

(10^{-1}) M $CuSO_4$ (aq) solution was prepared ($CuSO_4.5H_2O$ molar mass=249.68gmol^{-1}), 100ml of prepared (10^{-1}) M $CuSO_4$ (aq) solution was taken to a beaker, after sample has completed the set time in the oven to grow p-Cu_2O thin film, it is taken out and quenched in the $CuSO_4$ solution taken to the beaker. Samples were kept in the $CuSO_4$ solution for 6h, 12h, 24h and

48h before taken out, cleaned using distilled water and then subjected to study their diffuse reflection spectrum and VI characteristic curves.

2.3 Experimental techniques:

Diffuse reflectance spectra of fabricated p-Cu_2O samples and n-Cu_2O QD sensitized Cu/p-Cu_2O samples were obtained using Shimadzu UV-visible 1800 spectrophotometer. Photochemical characteristics were obtained using HOKUTU DENKO HA-301 potentiostat/galvostat with three-electrode configuration having Pt as counter electrode and AgCl/Ag as the reference electrode, (10^{-2} M) KI (aq) solution was used as the electrolyte. All chemicals used for the experiment were analytical grade.

3. RESULTS AND DISCUSSION

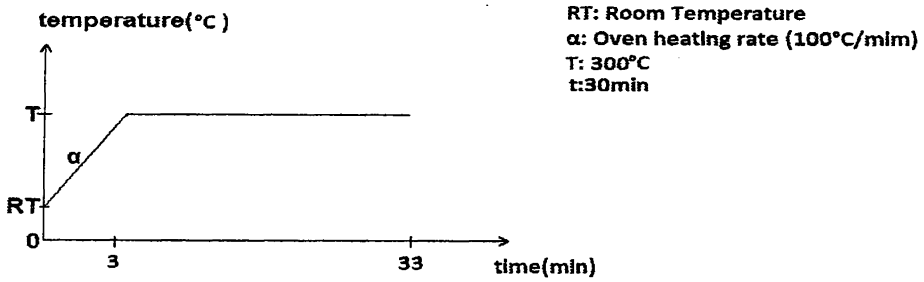

Figure 1: Temperature profile p-Cu_2O fabrication Method 1

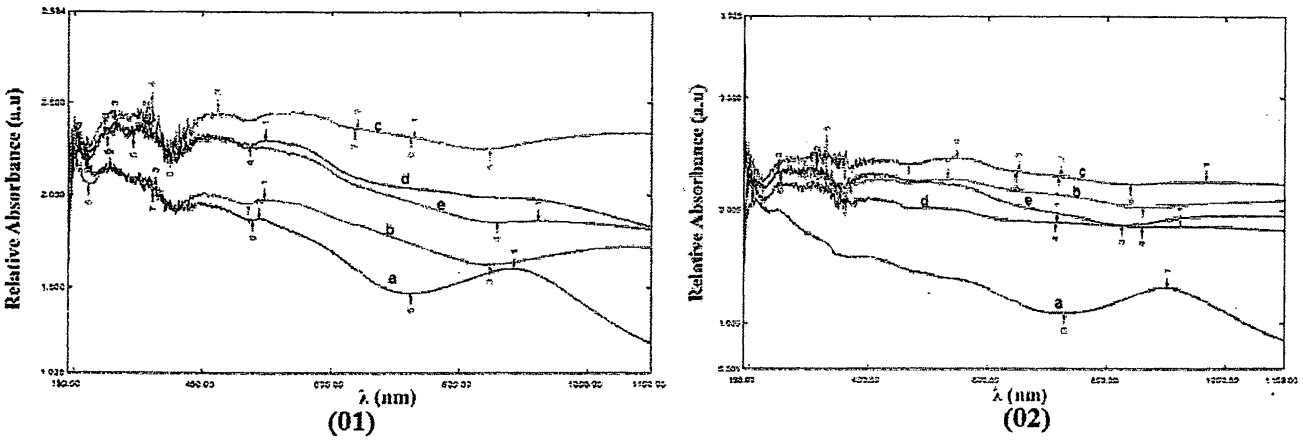

Figure 2: (01) Diffuse reflectance spectra of Cu/p-Cu_2O (p-Cu_2O thin film fabricated with 300°C time 30min)(a) Not (b) 6 h quenched, (c) 12 h quenched, (d) 24 h quenched and (e) 48 h quenched, (02) Diffuse reflectance spectra of Cu/p-Cu_2O (p-Cu_2O thin film fabricated with 900°C, time 1min 16sec) (a) Not quenched (b) 6 h quenched, (c) 12 h quenched, (d) 24 h quenched and (e) Cu/p-Cu_2O 48 h quenched

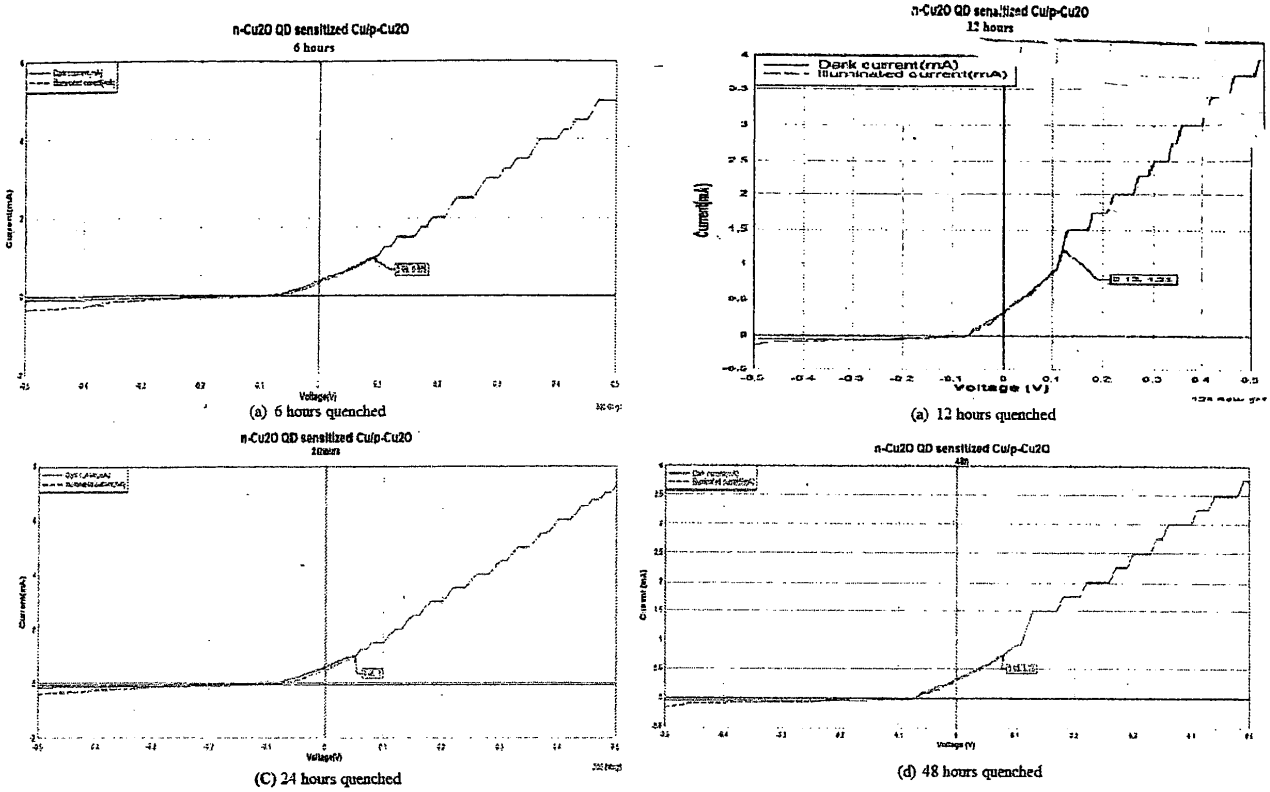

Figure 3: V-I characteristics of Cu/ p-Cu_2O/ n-Cu_2O QD for various quenching time periods (p-Cu_2O thin film fabricated in 300°C time 30min) in the presence of (10^{-2} M) KI/I_2 redox couple (dotted curves-illuminated current, solid curves-dark current)

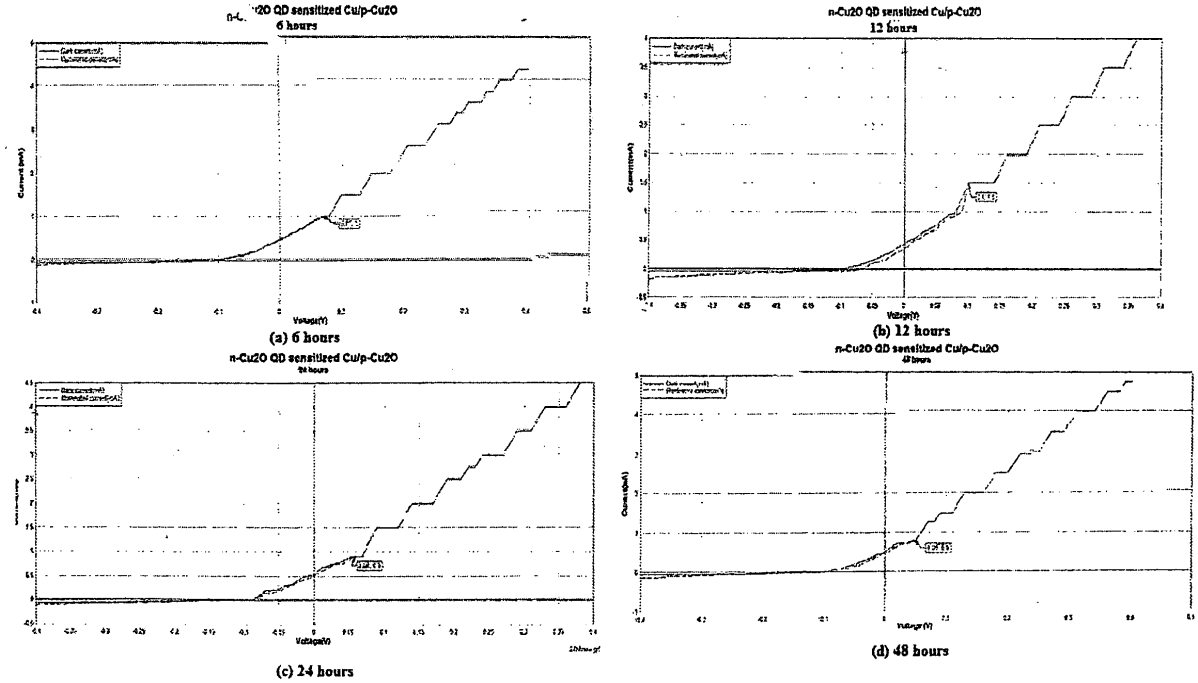

Figure 4: V-I characteristics of Cu/ p-Cu_2O/ n-Cu_2O QD for various quenching time periods (p-Cu_2O thin film fabricated in 900°C, time 1min 16sec) in the presence of (10^{-2} M) KI/I_2 redox couple (dotted curves-illuminated current, solid curves-dark current)

3.1 Sample characterization:

Brick red colored surface can be observed from the samples which were prepared using two thermal oxidation methods described in experimental section. It was visually confirmed that the yellowish brown Cu substrate has been changed to brick red fabricating p-Cu_2O layer on top. After quenching samples surface color turned in to grayish pink. Analysis of diffuse spectra of p-Cu_2O samples which were prepared with both methods displayed peak band edges between 630nm and 645nm.

Figure 2 (01) shows diffuse reflectance spectra of Cu/p-Cu_2O (fabricated with 300°C for 30min) quenched in (10^{-1}) M $CuSO_4$ (aq) solution for 6 hours, 12 hours, 24 hours and 48 hours. These quenched Cu/p-Cu_2O samples displayed a peak edges between 665nm (band gap 1.86 eV) and 690nm (band gap 1.80 eV). Analysis of diffuse reflectance spectra of quenched Cu/p-Cu_2O samples clearly shows that all quenched samples have some amount of p-Cu_2O.12 hour sample shows a broad symmetric peak which is clear sign of n-Cu_2O quantum dot formation. But when time is increased symmetric property vanishes with formation of bulk n-Cu_2O.

Figure 2 (02) shows diffuse reflectance spectra of Cu/p-Cu_2O (fabricated with 900°C for 1min and 16sec) quenched in (10^{-1}) M $CuSO_4$ (aq) solution for 6 hours, 12 hours, 24 hours and 48 hours. Quencehed Cu/p-Cu_2O samples displayed a peak edge between 650nm and 680nm. Same as the previous case diffuse reflectance spectrums show existence of both p-Cu_2O and n-Cu_2O quantum dots. Also in this sample set 12hours sample shows the most broad and symmetric peak which shows the existence of n-Cu_2O quantum dots.

3.2 V-I characteristics:

V-I characteristics of Cu/ p-Cu_2O/ n-Cu_2O QD for various quenching time periods (for p-Cu_2O thin films fabricated from both methods) are shown in Figure 3 and Figure 4. Shape of the dotted and solid curves show typical V-I characteristics under dark and illumination. V-I characteristics studies were carried out in the presence of KI/I_2 redox couple. Results are shown in Table 1.

Table 1. On-set potentials and on-set currents for all quenched samples

Quenched time (hours)	For p-Cu_2O prepared with temperature profile 300°C, time 30min		For p-Cu_2O prepared with temperature 900°C, time 1min 16sec	
	On-set potential (V)	On-set current (mA)	On-set potential (V)	On-set current (mA)
6	0.09	0.975	0.07	1
12	0.12	1.25	0.1	1.5
24	0.05	1	0.06	0.9
48	0.08	0.75	0.05	0.8

From quenched p-Cu_2O samples which were prepared from both methods, 12 hours quenched samples show the highest on-set potential and the on-set current.

4. CONCLUSION

Method to fabricate n-type Cu_2O quantum dots on p-type Cu_2O thin film discussed in this study is simple and cost effective. Before fabricating n-type Cu_2O on p-type Cu_2O film, two different methods were used to fabricate p-type Cu_2O. P-type Cu_2O fabricated in both methods showed a direct band gap around 1.9eV. 12 hours quenched sample in both methods displayed the best results for existence of n-type Cu_2O quantum dots on p-type Cu_2O thin film.

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