NANOTECHNOLOGY WITH RAPID PHOTOTHERMAL PROCESSING FOR THIN FILM SOLAR CELLS

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ABSTRACT

Nanotechnology with Rapid Photothermal Processing (RPP) and successive ion layer adsorption and reaction (SILAR) has been developed to prepare ZnO, TiO_2 and Cu_2O nanostructures for solar cells applications. Nanostructured ZnO, TiO_2 and Cu_2O with an average size of about 200, 100 and 300 nm, respectively were synthesized, depending on synthesis conditions, using precursors ZnOH and $Cu(OH)_2$ and RPP for formation of properties of nanostructures for solar cells applications. The variations of nanostructural parameters with SILAR deposition and RPP annealing conditions are studied. The experimental results shown that by RPP is possible to control the surface morphology, electrical properties and photoluminescence of nanostructured zinc oxide thin films as active component and antireflection coating of the solar cells.

1. INTRODUCTION

Transparent semiconducting oxides are widely used as transparent electrodes in optoelectronic devices and solar cells. ZnO is a wide direct band gap semiconducting oxide with band gap energy of 3.3eV and a large exciton binding energy 60 meV. ZnO is intensively investigated to possible applications in electrical and optical devices, solar cells and light emitting diodes [1-5]. However, it is difficult to prepare a high quality ZnO semiconducting nanostructures by low cost methods. Besides seeking an effective method for high-quality ZnO fabrication heterojunction with *p*-Si, Cu_2O has become attractive. Heterostructure - based semiconducting devices exhibit enhanced carriers confinement compared to heterojunctions and these leads to higher device performance. *p*-type Cu_2O film can combine with *n*-type transparent semiconducting oxide ZnO or *n*-Si to form heterojunction, which provide a route for the realization of optoelectronic devices and in special for solar cell applications. Several *p*-type materials, having delafossite structure of $CuAlO_2$ have been reported ($CuYO_2$, $CuAlO_2$, $CuScO_2$ etc.) [6-7], were according to the guidelines for energy band engineering. Among these materials, cuprous oxide having similar electronic structure is selected as a *p*-type semiconducting oxide in this research. This is because Cu_2O is an attractive low-cost non-toxic material with potential applications in solar cells, sensors [8-11]. The theoretical energy conversion efficiency of Cu_2O solar cells is on the order 20% [12]. Also the preparation of Cu_2O films at low temperatures is of much interest because deposited films are also expected to have reduced defect formation arising from thermally induced stresses as compared to high temperatures deposited films.

TiO_2 films are extensively studied because of their interesting chemical, electrical and optical properties. TiO_2 is a high bandgap semiconductor that is transparent to visible light and has excellent optical transmittance. TiO_2 has high refractive index and good insulating properties, and as a result it is widely used for manufacture of integrated circuits, optical elements, dye-sensitized photovoltaic cells as well as antireflective (AR) coatings, gas sensors, electrochromic displays, and planar waveguides. The high dielectric constant of TiO_2 allows its consideration as an alternative to silicon dioxide for ultrathin gate oxide dielectrics used in memory and logic devices. RPP technology is attractive for solar cells and microelectronic fabrication [13-18].

In this study, we prepared ZnO, TiO_2 and Cu_2O nanostructures using nanotechnology with SILAR deposition and RPP method. Compared with other technological routes, our method presents several advantages such as: low-temperature deposition, arbitrary substrate relief, controllable film thickness, morphology, parameters, rapid photothermal processing, possibility to fabricate multilayer heterostructures and potentially low-cost.

2. EXPERIMENTAL

In this work both ZnO and Cu_2O nanostructures were prepared by SILAR method. In order to attain 0.12M aqueous zinc complex solution was utilized zinc sulphate, natrium hydroxide and deionized water. The addition of ethanolamine enhances the wetability of substrates and ensures a controlled deposition. These CDA Reagent grade chemicals were mixed to reach homogeneity and clean glass and Si substrates were immersed into zinc complex solution which was kept at 65 ºC to speed up the reaction. As a result $Zn(OH)_2$ precipitate was formed on substrates by the following reaction [19]:

$$Zn^{2+} + 2OH^{-} \longrightarrow Zn(OH)_2 \ , \quad (1)$$

where Zn^{2+} ions come from Zn complex solution and OH^- from anionic bath. After the depositions the nanostructures was dried at 150 ºC for 5 min prior to RPP and characterization.

In the case of cuprous nanostructures preparation cleaned glass substrates (glass, Si) were immersed into complex solution of $3Cu_2S_2O_3 \cdot 2Na_2S_2O_3$ kept at room temperature and then into hot 4M NaOH at 70 ºC. The global reaction is:

$$CuSO_4 + Na_2S_2O_3 \rightarrow 3Cu_2S_2O_3 \cdot 2Na_2S_2O_3. \ (2)$$

The dipping was repeated periodically and Cu_2O nanostructures were deposited on substrate. The mechanisms scheme of the deposition process consists of next consecutive steps: the reaction of dissolved precursors of the halogen and the metal at the substrate surface (heterogeneous chemical), and then the deposition by diffusion of precipitates and clusters formed in solution. After deposition the substrates were dried in air for 5 min in N_2 flux.

The sol-gel technique has emerged as one of the most promising techniques to prepare titania films as this method produces samples with good homogeneity at low cost. Chemically and thermally stable films of TiO_2 were prepared using the Sol-Gel technique. In this case consists of suspension of the metall-organic compound Titanium Isopropoxide. The route to preparation of the TiO_2 films begins with the three starting materials Titanium Isopropoxide, Glacial acetic acid and ethanol. Acetic acid is first added to 50mls ethanol and allowed to mix for 5 minutes. Subsequently, TIP is added to the mixture in a molar ratio of 4.16:1 TIP:ACID. After the solution has been stirred for 2 minutes ultrsonically cleaned substrates of ITO coated glass and Fluorine doped Tin oxide glasses were dipped into the sol at a dip speed of 250mm/min. The films were left to dry in air for 24 hours then heated under atmospheric conditions to 500°C for 5 hours [13].

X-ray diffraction analysis on residues of the sol mixture have revealed for gels heated to 100°C the structure is predominantly amorphous, however gels heated to 500°C show that anatase is the predominant structure.

Systematically, the first sample of ZnO (and Cu_2O) is not annealed and the four other ones are RPP annealed in vacuum at different temperatures ranging from 200 to 500 ºC during 20 sec using lamp-based photoassisted rapid photothermal processing set-up described in [8].

EDX patters of the as-prepared and RPP annealed samples were recorded on an EDX spectrometer. The optical transmittance (T, %) and near normal reflectance (R, %) spectra were recorded on spectrophotometer with air and a front aluminized mirror, respectively, referenced. The electrical properties were measured by two-point probe method where used ohmic contacts ensured by the Al film vacuum evaporated.

The TiO_2 thin films and heterostructures TiO_2/organic have been prepared by sol-gel technology [13].

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the impact of RPP treatment on the surface morphology of a ZnO chemically deposited under UV irradiation from zinc complex solution. A continuous coverage of the substrate surface is observed in Fig 1.

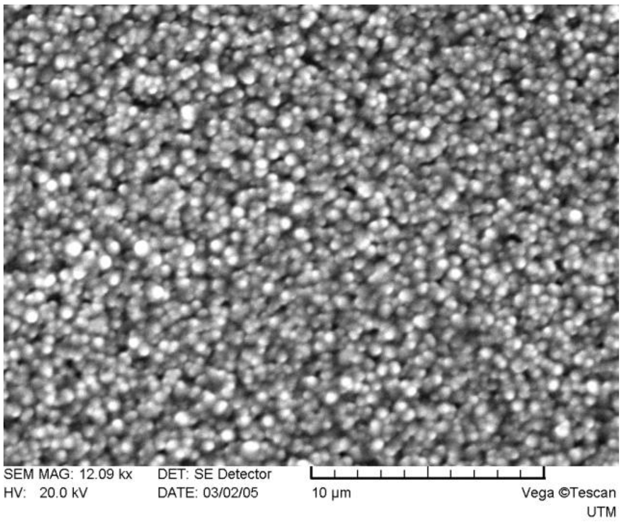

Figure 1. SEM micrograph of ZnO nanocrystals deposited on Corning glass substrate precipitated from an aqueous zinc complex solution 0.12 M irradiated UV with 100W power. Samples were subjected to RPP at 650 °C, 20 sec.

Fig. 2 shows the impact of RPP treatment on the surface morphology of a Cu_2O chemically deposited under UV irradiation from cuprum complex solution. The as-grown Cu_2O microcrystallites mean size is ~200nm. RPP leads to the decrease of the grain sizes by a factor of 1.5 [20].

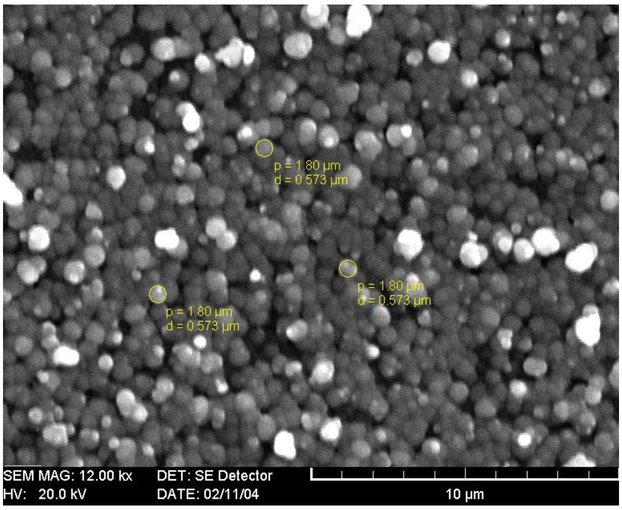

Figure 2. SEM micrograph of Cu_2O nanocrystals deposited on Corning glass substrate precipitated from an aqueous complex solution of $3Cu_2S_2O_3 \cdot 2Na_2S_2O_3$ irradiated UV with 100W power. Samples were subjected to RPP at 300 °C, 7 sec.

The composition of films and the atomic ratio of metal and O in the grown films have been investigated by the EDX measurements made in the plan detection mode. The diameter of the focused electron beam in EDX analyses is about 4 µm and the beam is scanning the films surface area of (50µm×50µm). The penetrated depth of focused high-energy electron beam is about 2 µm. The Zn:O and Cu:O ratio surveyed was 1:1 and 2:1, respectively, with an experimental error of about 10 % due to the small thickness of Cu_2O film compared with the high-energy electron beams penetration depth in EDX.

EDX analysis shows that RPP at temperatures higher than 300 °C lead to formation of Cu_xO_y and reduction of Cu:O ratio from 2:1 to 1:1 in dependence of processing regime.

The nanocrystalline Cu_2O films chemical deposited were RPP at 250°C, 300°C, 350°C, 425°C for 5÷100 sec. The optimum duration of RPP was determined as 7 sec for Cu_2O films. There is no apparent change in the morphologies of films annealed bellow 300°C. However, the color change has been observed for the films annealed at 375-425°C. The rapid photothermal processing in air at a temperature above 300°C therefore causes the oxidation of Cu_2O films.

To study the electrical characterization of the ZnO and Cu_2O films, electrical resistivity measurements were performed using two-point probe method in the temperature range 300-480K. Figure 3 shows dependence of the electrical resistivity of a zinc oxide films versus rapid photothermal processing RPP regime.

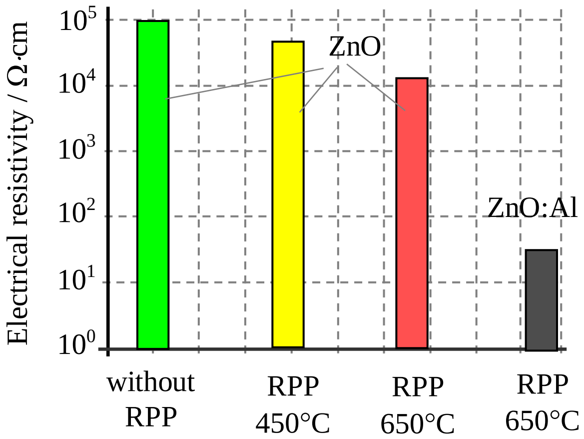

Figure 3. Electrical resistivity of a zinc oxide films versus rapid photothermal processing RPP regime.

The type of conductivity exhibited by obtained semiconducting oxide thin films was determined by thermoemf measurements. The polarity of thermally generated voltage at the hot end is positive indicating the *n*-type for ZnO films and the *p*-type for Cu_2O films.

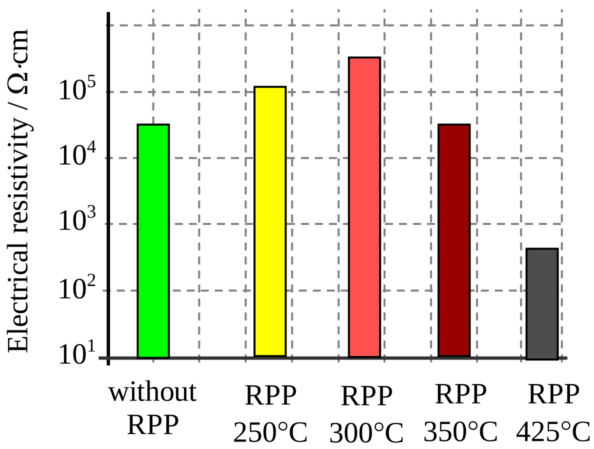

Figure 4. Electrical resistivity of a cuprous oxide films versus rapid photothermal processing RPP temperature.

The room temperature resistivity of the Cu_2O films as prepared and annealed at different

RPP temperatures was measured. The resistivity of the Cu_2O films as prepared is $6{\cdot}10^4$ Ω·cm, but that of the Cu_2O films after RPP at 250°C, 300°C, 350°C and 425°C for 7 s is, respectively, $2{\cdot}10^5$ Ω·cm, $6{\cdot}10^5$ Ω·cm, $4{\cdot}10^4$ Ω·cm and $6{\cdot}10^2$ Ω·cm (see Fig. 4). It is clear that RPP annealing increases the resistivity of Cu_2O films for temperatures up to 300°C and decreases for higher temperature, which may be due to increase in hole conduction. The Cu_2O thin films were further analyzed in order to identify the applications as transparent materials in solar cells applications.

Figure 5 shows the transmittance of chemical Cu_2O films RPP annealed at 250°C, 300°C, 350°C, 425°C for 7 sec, along with that of an as prepared sample.

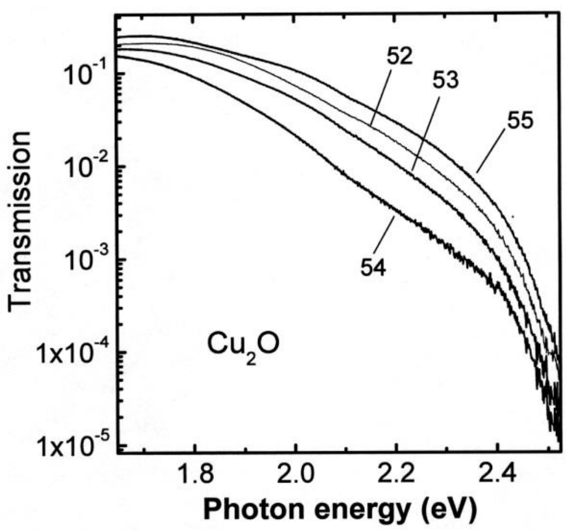

Figure 5. Transmittance as a function on photon energy of Cu_2O films: sample 55 – initial, 52 – after RPP at 300°C, 53 – after RPP at 350°C, 54 – after RPP at 425°C with duration 7 sec.

With the decreasing wavelength of radiation, the transmittance of all samples tended to be lowered. In the case of an annealing temperature of 300°C, the transmittance of the film is found to be better compared to that of other samples. The absorption coefficient satisfies the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for a direct band gap material. The band gap (E_g) was obtained by extrapolation of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ and is found to be 2.05 eV for as-grown films.

The bath temperature and pH have direct effect on the composition and microstructure of the Cu_2O films [21].

Figure 6 shows the absorption spectra of Sol-Gel deposited TiO_2 and CuPc films. As is seen in Figure 6 TiO_2 is full transparent and in combination with organic and nonorganic semiconductors can produce photovoltaic effects.

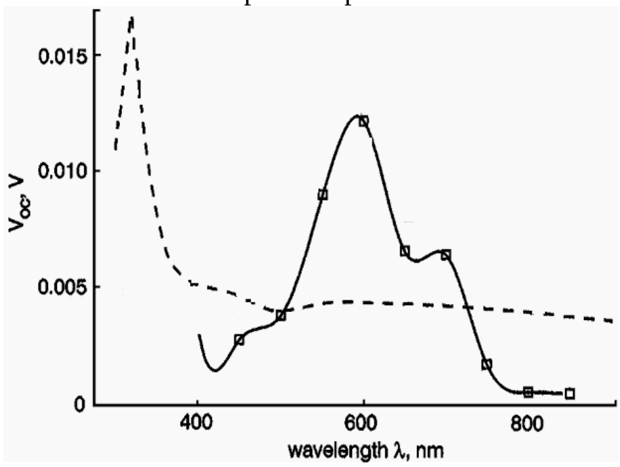

Figure 6. Absorption spectrum of the titanium dioxide TiO_2 and CuPc.

The response indicates that the photovoltaic effects arise from light absorption in the CuPc dye layer and separation of the photoexcited carriers at the CuPc dye/TiO_2 interface.

Current-voltage (*I*-*U*) characteristics (fig. 6) were performed at room temperature using Measure Unit of Semiconductor Devices Characteristics "Л2-56" under simulated AM1 solar spectrum (PRM 500 Watt Xenon lamp, Model Number 20101).

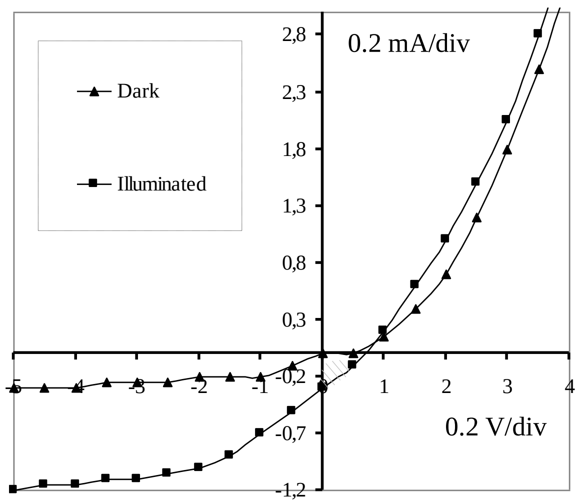

Figure 7. Current-voltage characteristics of the analyzed ZnO/Si – based solar cells. The illumination was performed using an AM1.5 solar simulator (PRM 500 Watt Xenon lamp, Model Number 20101). The illuminated characteristics of

the element (B) were measured at an illumination intensity $P_{ill} = 100\, mW / cm^2$.

It was found that all ZnO/Cu_2O and ZnO/*p*-Si heterojunction devices fabricated using ZnO and Cu_2O films deposited by SILAR exhibit rectifying current-voltage characteristics. The variation found in the *I-V* characteristics can be caused by changes in the electrical properties of the *n*-ZnO layer and *p*-Cu_2O layer as well as interface region between these layers. The improvement shown in rectifying characteristic may be assigned to a reduction of defects in the films after RPP.

3. CONCLUSIONS

In this work, we report the chemical deposition of nanocrystalline ZnO and Cu_2O films, and Cu_2O thin films on ZnO films coated on transparent optically glass. The bath temperatures and pH have strong effect on the composition and microstructure of thin films. RPP annealing in low vacuum and in air at a temperature above 300°C causes the oxidation of Cu_2O and decreases the electrical resistivity of nanocrystalline Cu_2O thin films. Optical absorption measurements indicate that RPP at 300°C, 7s can improve the transmittance of nanocrystalline Cu_2O thin films.

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