Investigation of a p-CuO/n-TiO$_2$ thin film heterojunction fabricated by the sol-gel process

N. YILDIRIM*, T. SERIN, N. SERIN
Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Tandoğan, Ankara, Turkey.

The p-CuO/n-TiO$_2$ thin film heterojunction is fabricated by the sol-gel technique on the glass substrate coated ATO (antimony doped tin oxide). The crystallinity of the junction materials is examined by an x-ray diffractometer (XRD). The electrical characterizations of the p-CuO/n-TiO$_2$ heterojunction were measured by means of the current–voltage and capacitance-voltage measurements at room temperature. It was observed that the junction between p-CuO and n-TiO$_2$ was rectifying. It was determined that the ratio of forward current to the reverse current was about 139.9 at 1.5 V and the diode ideality factor was much greater than 2. The forward turn-on voltages were about 0.5 V. In order to analyze the electrical properties an energy-band diagram was proposed, it was deduced from the current–voltage measurements that the turn-on voltages were smaller than the barrier potentials which exhibited the existence of the interface defect states. The mechanism of charge transportation was discussed and a tunnel recombination process was proposed to explain its electrical properties.

1. Introduction

In recent years, there was considerable interest in the coupling of two kinds of semiconductor materials with different energy band gap. Such systems have the modified characteristics of charge transport and thus have potential applications in many aspects, such as solar cells, photochemical energy storage, photo catalysis and nano-electronics, etc [1]. Wide band gap semiconductor materials (2.5-3.5 eV.) are typically more stable compared to narrow band gap (0.8-2 eV.) materials; however, the solar spectrum is more efficiently absorbed by the narrow band gap materials. Thus, it has been reported previously that heterojunction consisting of narrow gap semiconductors as light absorbers and wide gap semiconductors as stabilizers can be prepared for applications [2].

TiO$_2$ is a well-known n-type oxide semiconductor available in various forms such as brookite; anatase and rutile structure has been subject of optoelectronic device applications. TiO$_2$, a wide band gap material, can be chemically activated by various techniques like organic precursor decomposition, chemical vapour deposition, sputtering, spray pyrolysis screen-printing techniques and sol-gel method. Since it is low cost the most researchers prefer the sol-gel method [3,4].

In this study, it was planned to use CuO which have a direct band gap of 1.85 eV as a narrow band gap and p-typed material as a hetereo junction of TiO$_2$. It was aimed to fabricate p-CuO/n-TiO$_2$ heterojunction and to measure the current–voltage and capacitance-voltage characterization at room temperature. In order to analyze the electrical properties of the hetereojunction an energy-band diagram was proposed.

2. Experimental

The TiO$_2$ solution used for the dip-coating was a mixture of tetraisopropylorthotitanat (C$_{12}$H$_{26}$O$_4$Ti), ethanol, acetic acid and triethylamine. First a quantity of C$_{12}$H$_{26}$O$_4$Ti (1.2 ml) was added to ethanol (50 ml). While stirring the solution vigorously at room temperature, glacial acetic acid (5 ml) was added to it. Finally triethylamine (1.5 ml) was added as a pH regulator. The composition was stirred for 2 h continuously and finally TiO$_2$ transparent sol was obtained. Crack free films were formed on the ATO-coated glass substrates by dipping it in to the TiO$_2$ sol and pulling it up at a constant rate of 0.4 mm/sec by employing micro controlled stepper motor setup. These dipped substrates were then dried at 250 °C for 5 min and the process was repeated for multiple coatings. The films were then sintered at 500 °C for 15 min.. In order to prepare the CuO solution, 2.5 g cupric acetate was dissolved in 100 ml ethanol by heating. Then, the solution was stirred vigorously for 2 h. When it was mixing, lactic acid was added as a catalyst and triethylamine was added as a pH regulator. The substrates were again dipped at the same constant velocity in to the CuO sol as the TiO$_2$ sol. This dipped substrates were then dried at 250 °C for 5 min and the process was repeated for ten times. Finally, the films were then sintered at 250°C for 15 min. After these processes, CuO layer was also deposited by sol-gel dip-coating method on TiO$_2$.

In order to investigate the structure of the deposited films the X ray diffraction studies were carried out with a Rigaku D/Max 2200 diffractometer, CuK$_\alpha$ radiation with a wavelength 0.154 nm was used and the scanning range of 2θ was restricted to the range 20-60° (Fig.1). In order to determine the optical band gap of the material of the films transmittance measurements were performed by Shimadzu

UV-3600 in the spectral range of 300-1100 nm. The current–voltage (I–V) measurements were performed by means of a Keithley 2420 Current-Voltage Source. The C–V measurements were also performed by HP 4192A impedance analyzer. All the measurements were realized at the room temperature and in the dark.

3. Results and discussion

The XRD pattern of the heterojunction is shown in Fig. 1. This revealed the crystalline nature with crystals oriented (101) plane of the anatase phase of the TiO_2 [5] and monoclinic tenorite CuO phase [6]. The optical property of the TiO_2 and CuO films are investigated by means of the transmission spectra. According to the transmission spectra, the optical band gaps of TiO_2 and CuO were determined by plotting $(\alpha h\nu)^n$ versus $h\nu$ where n was equal to ½ and 2 for direct band-gap (CuO) and for indirect band gap (TiO_2), respectively Fig. 2. The linear portion of the curve was extrapolated. The intercept of $h\nu$-axes gave energy-band gap of the materials. The energy band gaps of TiO_2 and CuO were found 3.4 and 1.85 eV, respectively.

The energy-band diagram of the heterojunction was proposed by means of the measured band gaps of TiO_2 and CuO and I-V characteristic was explained by the proposed energy-band diagram in Fig. 3. The proposed energy band diagram provides an estimate the value of contact potential of p-n heterojunction. The built-in potential is the difference between the work functions of the two semiconductor materials. The affinity of CuO and TiO_2 are 4.07 eV [7] and 4 eV [8], respectively. Fig. 4 presents the Arrhenius plots at 340-390K of dc conductivity of CuO and TiO_2 films. The conductivity is given as $\sigma=\sigma_0 e^{-EA/kT}$, where E_A is the activation energy . The activation energies were obtained from the slopes by best fitting to 0.294 eV for CuO and 0.694 eV for TiO_2. Although film preparation methods are different these values are quite comparable with the reported values [9] for CuO and [10] for TiO_2. The work functions of CuO and TiO_2 were calculated as 5.626 eV and 4.694 eV and the built-in potential is found as ~0.932 eV.
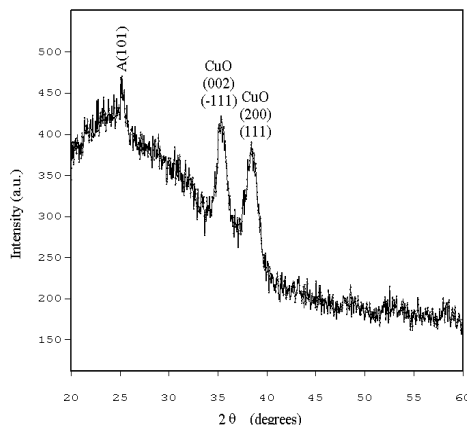
Fig. 5 shows schematic diagram of the p-CuO/n-TiO_2 heterojunction and its typical I-V characteristic at room temperature. It is obviously seen that structure has a quite good rectifying behaviour. The ratio of the forward current (I_F) to the reverse current (I_R) was obtained as about 139.9 at 1.5 V. The forward turn-on voltage of the heterojunction was found as 0.5 V. The turn-on voltage, also identified as the diffusion or built in potential corresponds to a potential barrier which carrier has to overcome in order to contribute to forward current [11]. The forward current-voltage relationship [12] is given by

$$I = I_s \, \exp(qV/nkT) \qquad (1)$$

where I_s ,V, k, n, q and T are the saturation current, the applied voltage, the Boltzmann constant, the ideality factor, the electronic charge and absolute temperature, respectively. The ideality factor value was obtained as 4.6 from the slope of the plot of lnI versus V (Fig. 6). Since the ideality factor is quite larger than an ideal p-n junction, the ideal I-V model can not explain the current transport mechanism of the heterojunction [13].
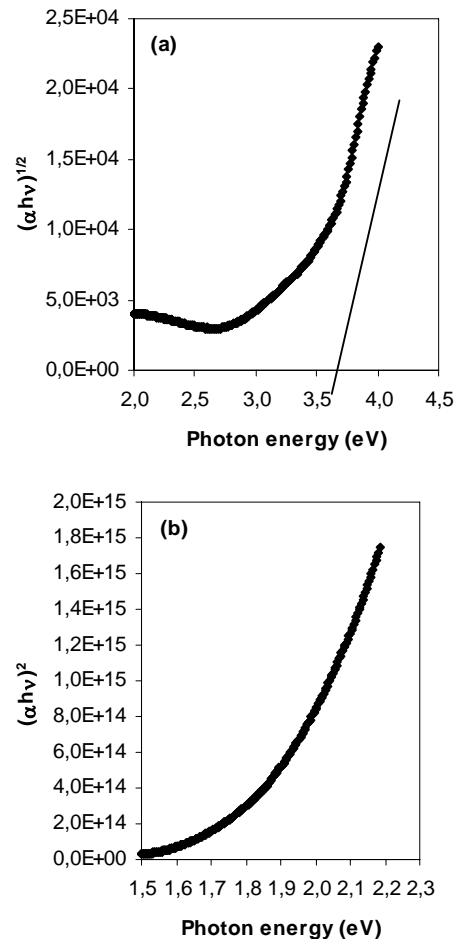

Fig.1. XRD pattern of the p-CuO/n-TiO_2 heterojunction on the glass substrate.

Fig. 2. Graphical determination of the optical band gap from the transmission spectra of (a)TiO_2 and (b) CuO thin films.
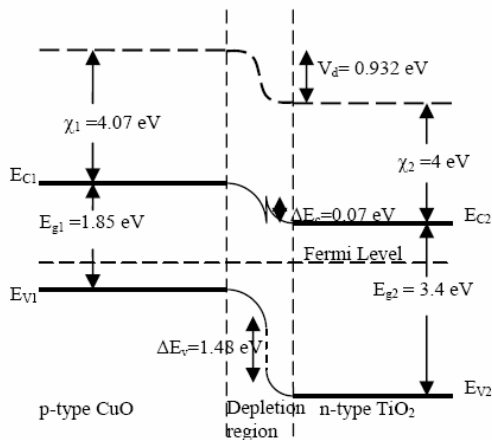
Fig. 3. Energy band diagram for the p- CuO /n- TiO₂ heterojunction in equilibrium.

The capacitance per unit area of abrupt p-n heterojunction is given by [12]

$$C = \left[\frac{q\varepsilon_1\varepsilon_2 N_1 N_2}{2(\varepsilon_1 N_1 + \varepsilon_2 N_2)} \right]^{1/2} (V_D - V)^{-1/2} \qquad (2)$$
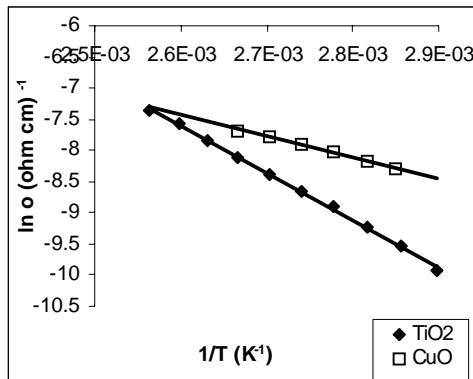

Fig. 4. Temperature dependence of the conductivity for TiO₂ and CuO films.

where ε_1, ε_2, N_1, N_2, V_D and V are the dielectric constants of the semiconductors, the carrier concentrations, the built-in potential and the applied voltage, respectively. The built in potential is found as 0.9 V from capacitance-bias voltage (Fig 7) agreement between that value and the value obtained from the energy-band diagram of the structure.   The turn-on voltage obtained from I-V characteristics is smaller than the barrier potential and ideality factor of the structure is greater than 2. These results exhibited the existence of the interface defect states. Due to the large mismatch of the lattice constant between CuO and TiO₂, there must be many interface states in the depletion layer, which can play important role in the charge transport process. Therefore ideal model can not explain the current transport mechanism in the

hetereojunction. It appears that there is multiple   transport mechanism such as defect-assisted multi-step tunnelling and carrier recombination in the space charge region via interface states.
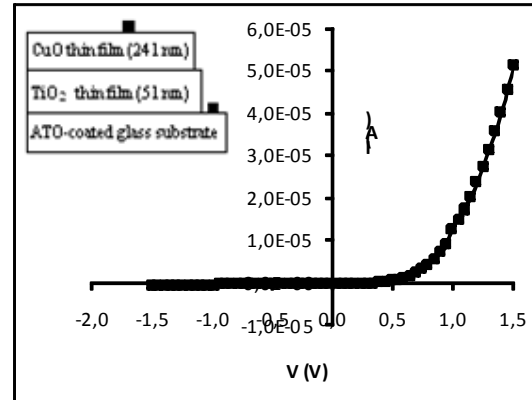

Fig. 5. I-V characteristic for p-CuO/n-TiO₂ heterojunction at room temperature. The inset is the schematic diagram of heterojunction.
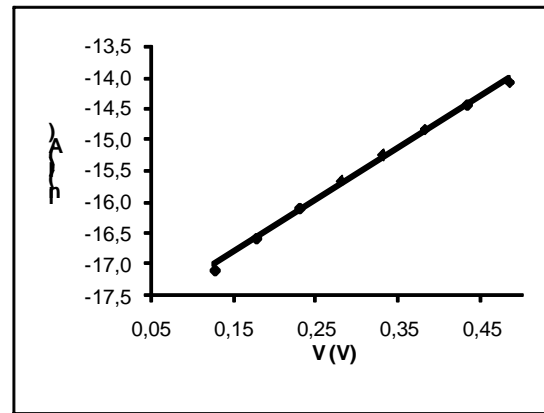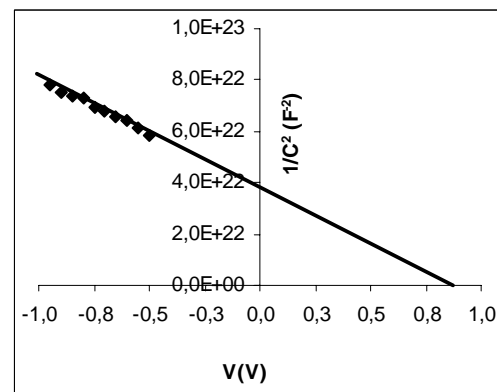

Fig. 6. The plot of lnI versus V for ideality factor.

Fig. 7. Variation of 1/C² with bias voltage at 1 MHz for CuO/TiO₂ heterojunction at room temperature.

4. Conclusions

The p-CuO/n-TiO$_2$ thin film heterojunction was fabricated by the sol-gel process and the electrical characteristics were measured. It was observed that p-CuO/n-TiO$_2$ hetero junction has the rectifying behaviour. The ratio of forward current to the reverse current was about 139.9 at 1.5 V. The diode ideality factor was much greater than 2. The forward turn-on voltage was about 0.5 V. The smaller turn-on voltage is due to the tunnel recombination process that is based on existence of the interface states in CuO and TiO$_2$.

References

[1] Z. Liu, W. Guo, D. Fu, W. Chen, Synthetic Metals **156** 414 (2006).
[2] W. Siripala, A. Ivanovskaya, T. F. Jaramillo, S. Baeck, E. W. McFarland, Sol. Energy Mater. Sol. Cells **77**, 229 (2003).
[3] G. D. Sharma, V. S. Choudhary, M. S. Roy, Sol. Energy Mater. Sol. Cells **91**, 1087 (2007).
[4] S. Senthilarasu, R. Sathyamoorthy, S. Lalitha, A. Subbarayan, Sol. Energy Mater. Sol. Cells **90**, 783 (2006).
[5] M. M. Rahman, K. M. Krishna, T. Miki, T. Soga, K. Igarashi, S. Tanemura, M. Umeno, Sol. Energy Mater. Sol. Cells **48**, 123 (1997).
[6] T. Maruyama, Sol. Energy Mater. Sol. Cells **56**, 85 (1998).
[7] G. Mangamma, V. Jayaraman, T. Gnanasekaran, G. Periaswami, Sensors and Actuators B **53**, 133 (1998).
[8] Q. Fan, B. McQuillin, D.D.C. Bradley, S. Whitelegg, A. B. Seddon, Chemical Physics Letters **347**, 325 (2001).
[9] U. D. Lanke, M. Vedawyas, Nuclear Instruments and Methods in Physics Research B **155**, 97 (1999)
[10] K. Romoni A.Vamvas, Chr. Trapolis Thin Solid Films **516**, 1272 (2008)
[11] R. S. Ajimsha, K. A. Vanaja, M. K. Jayaraj, P. Misra, V. K. Dixit, L. M. Kukreja, Thin Solid Films **515**, 7352 (2007).
[12] S. M. Sze, Physics of Semiconductor Devices, John Wiley and Sons, Newyork, 1981.
[13] S. Mridha, D. Basak, Semicond. Sci. Technol. **21,** 928 (2006).

_____
[*]Corresponding author: nurcanyil@gmail.com