Journal of Alloys and Compounds 617 (2014) 602–608

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Rectifying structure with high voltage operation based on $CuBO_2$ as an UV photocatalyst

M. Soylu [a],*, Ahmed A. Al-Ghamdi [b], Saad Bin Omran [c], F. Yakuphanoglu [b,d]

[a] Department of Physics, Faculty of Sciences and Arts, Bingol University, Bingol, Turkey
[b] Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[c] Department of Physics and Astronomy, College of Science, King Saud University, Riyadh, Saudi Arabia
[d] Department of Physics, Faculty of Science, Firat University, Elazig 23169, Turkey

ARTICLE INFO

Article history:
Received 28 May 2014
Received in revised form 25 July 2014
Accepted 5 August 2014
Available online 13 August 2014

Keywords:
Heterojunctions
Sol–gel synthesis
X-ray diffraction
Light absorption and reflection

ABSTRACT

$CuBO_2$/p-Si diode is a new rectifying structure with photosensing, which is a candidate for producing high voltage protection circuit in electronic application. It has been seen that the photocurrent in the reverse bias I–V characteristic is strongly increased by photo-illumination. It is believed that the combination of thin $CuBO_2$ layer and p-Si will provide high voltage protection level, which does not exist for conventional Si diodes. The capacitance and conductance–voltage characteristics were measured at various frequencies. The results indicate that the electrical parameters of $CuBO_2$/p-Si diode are affected by the series resistance and interface states. The optical properties of the $CuBO_2$ thin film were analyzed by UV–vis–NIR spectrophotometry and FTIR studies. The optical band gap of the $CuBO_2$ is located in the ultraviolet (UV) range. In this spectral range, the B—O—B bonds and relationship between Cu^{2+}–O are confirmed.

1. Introduction

The transparent oxide materials are important for electronic applications because of their optical transparency in the visible region and interesting electronic properties [1,2]. The photovoltaic applications are being developed using transparent conducting films [3–6]. The hole localization around oxygen owing to the large electro-negativity of oxygen in oxide compounds limits the hole mobility. In order to solve the problem, Cu based delafossites were synthesized. The $CuBO_2$, which is one of the members of the Cu-delafossite family such as $CuXO_2$ (X = A1, Ga, In), is a p-type transparent oxide. $CuBO_2$ that has electrical conductivity of 1.65 Scm^{-1} at room temperature exhibits the highest intrinsic conductivity with respect to delafossites [7]. The methods such as combustion [8], hydrothermal [8], sputtering [9] and pulsed laser deposition (PLD) [10] were performed to obtain the $CuXO_2$. The high temperature methods are not appropriate because boron is a volatile element. Scanlon et al. [11] reported a theoretical study on the p-type electrical conduction mechanism in $CuBO_2$. The lattice values obtained from experimental data for $CuBO_2$ were found to be highly questionable compared to a density functional theory. The direct band gap of the compound $CuBO_2$ estimated with the local density approximation (LDA) that is a theoretical approach yielded 3.52 eV [12]. The optical band gap of $CuBO_2$ is higher than compared to Cu based delafossite compounds. The mobility value measured for $CuBO_2$ with p-type conductivity was reported to be 100 cm^2/Vs in literature [7].

Metal oxide-silicon diode is a Schottky barrier diode with interfacial layer. The high-power devices can be obtained by oxide semiconductor based junction. In the electronic devices, when terminals are changed to the wrong way around, deterioration is inevitable. The potential barrier across a contact protects a circuit element (a radio or a recorder etc.), by preventing current to flow. Diodes can undertake this task at high voltages. However, the usage of diodes with high voltage operation has been limited due to the stability of interface between metal and semiconductor [13]. It is needed to develop the interfacial layer based Schottky diodes to operate and proceed successfully.

There are many studies of light-sensitive diodes in the literature [14–18]. It has been reported that Cu based transparent p-type semiconductor oxides have photocatalytic effect [19]. $CuAlO_2$ has attracted the interest in this regard. The optical properties like absorption and photoluminescence for this material have been analyzed by a variety of methods [20–22]. The usage of the various types of copper delafossites in the form of a contact provides a 'functional' window, which is transparent to the visible component of solar radiation. Thus, the absorption of the ultraviolet component of it is converted to electricity. In this study, thin films of $CuBO_2$ have been deposited on the glass and Si substrate using

---

* Corresponding author. Tel.: +90 426 2160012; fax: +90 426 2150877.
E-mail addresses: soylum74@yahoo.com, fizik.07@hotmail.com (M. Soylu).

http://dx.doi.org/10.1016/j.jallcom.2014.08.048
0925-8388/© 2014 Elsevier B.V. All rights reserved.

sol–gel spin coating method. The photovoltaic characteristics of $CuBO_2$/p-Si junction were investigated in high voltage of 10 V. As many electronic applications of silicon are widely reported in the literature [23–27], it would be considerable to study the combination of $CuBO_2$.

2. Experimental details

For the synthesis of $CuBO_2$ film, the used precursors are copper(II)-acetate monohydrate and boric acid. Nominal ratios of copper(II)-acetate monohydrate and boric acid were dissolved in deionized water and stirred for 5 h. Acetic acid was added to solution and was stirred at room temperature. The sol were achieved by adding ethyleneglycol and dimethylformamide. In order to clean the p-type silicon wafer having orientation of (1 0 0), RCA (Radio Corporation of America) method was used as well known standard procedure. Aluminum (Al) was thermally evaporated on silicon substrate for the formation of ohmic contact. Some of the solution was dropped onto silicon substrate and spinned at 1000 rpm for 30 s. The obtained coating was dried at 150 °C to obtain a solid film. The solid film of $CuBO_2$ was annealed at 500 °C for 4 h. The film thickness of the $CuBO_2$ film was determined using a XEI softwaring of PARK system Atomic Force Microscopy (AFM) and was found to be 120 nm. After coating of film layer, Al dots were deposited through molybdenum mask with contact area of 3.14 cm^2. Thus, $CuBO_2$/p-Si/Al heterojunction was obtained (Fig. 1). The morphology and optical properties of the $CuBO_2$ film were investigated. The heterojunction obtained was examined by *I–V* and *C–V* measurements.

3. Results and discussion

3.1. Illumination intensity dependence of the I–V characteristics

Fig. 2 shows the SEM image of sol–gel synthesized $CuBO_2$ (20,000× and 50,000× total magnification). The $CuBO_2$ film is formed from nanoparticles with various sizes of 70–80 nm and 280–400 nm. The most of particle sizes are in the range of 70–80 nm. The particle size distribution of the film on substrate is not homogeneous. The *I–V* flow rate across the $CuBO_2$/p-Si junction was measured using a semiconductor characterization system. The results are shown in Fig. 3. The black line represents no optical illumination. The structure indicates rectifying behavior at high voltage of 10 V in dark condition. The ideality factor and barrier height for the heterojunction diode were found to be 3.01 and 0.81 eV, respectively. Although the applied voltage is considerably high, the diode structure still maintains a rectifying behavior, which can be attributed to the large barrier height.

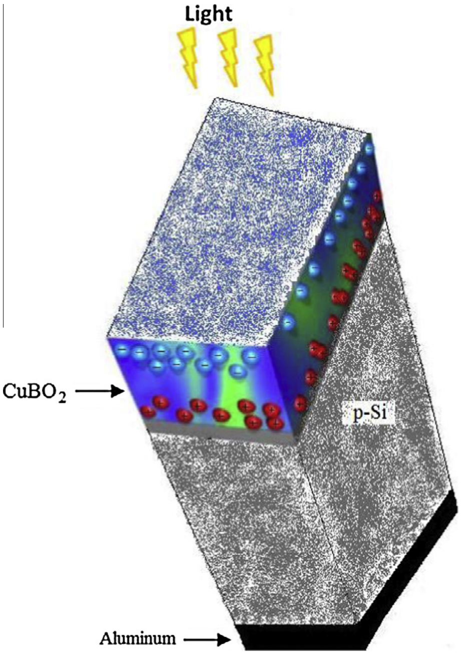

Fig. 1. The schematic diagram of $CuBO_2$/p-Si/Al heterojunction.

In the case of reverse biasing, the leakage current for the rectifying structure varies in response to the light intensity. With an applied reverse bias voltage, the current increases as the function of illumination intensity. If a junction is optically excited, an electron–hole pair, which is called exciton, is formed. The electron and hole in a steady state inject across the depletion region and then they move to opposite sides of the device, resulting an increase in reverse current. Thus, an extra current term take places in the *I–V* relation. The *I–V* relation through a rectifying structure is [28]:

$$I = I_0(e^{\frac{qV}{kT}} - 1) - \kappa P \tag{1}$$

where P is the illumination intensity, κ is a responsivity constant and changes in the range 0.1–0.5 mA/mW for visible light. In the case of I (=0), the diode voltage becomes as follow,

$$V = \frac{kT}{q} \ln\left(\frac{\kappa P}{I_0}\right) \tag{2}$$

The response in photocurrent (I_{ph}) to the same change in the optical power is not exactly linear, i.e. $\Delta I/\Delta P$ or the average absolute deviation (AAD). In the case of reverse bias voltage, Eq. (1) for photodiode is rewritten.

$$I = -I_0 - \kappa P \tag{3}$$

As the I_0 corresponds to the dark current, the second term is related to the illumination intensity. The photocurrent that is directly proportional to the light intensity is shown in Fig. 4. The corresponding equation is given as follow [29]:

$$I_{ph} = CP^{\beta} \tag{4}$$

where I_{ph} is the photocurrent, C is a constant, β is an exponent that must be experimentally calculated and P is the light intensity. β, derived from the photocurrent and light intensity was determined to be 0.70 ± 0.01. It seems to be in which a continuous distribution of localised trap levels is present. The better value of β, obtained for the device having the $CuBO_2$ thin film, implies a more perfect crystal structure and lower unfilled trap levels [30–32].

The transient photocurrent measurements for photoconduction mechanism in $CuBO_2$/p-Si diode are examined for different light intensities. The results are shown in Fig. 5a and b. The photocurrent starts to increase when the light on is set. The initial increase in the photocurrent can be attributed to the generation of exciton that is a bound state of an electron and a hole. Although the illumination remains constant between ten and twenty seconds, it is observed that the photocurrent is unchanged during the exposure time. It means that the saturation in the photocurrent is a limit in the light absorption within the $CuBO_2$ film. The plot of transient photoresponse is entirely different from the illumination dependence of the *I–V* characteristic, which exhibits a saturation in the photocurrent. The photocurrent decreases when the light is off. Note that the decrease mentioned is associate with the trapping of the electrons or holes at deep states. It is mentioned from the dark diode current, when all of the photo-induced carriers pile up on the device. The photoresponse is really a reflection of the conversion activity of the incident photon into photo-induced current. Liu et al. [33] have stated that the minority carrier lifetime, which is derivable from the photocurrent transient characteristic, affects the photo-sensing performance. While the photo-induced current increases with the increasing illumination intensity, the shape of the transient remains unchanged. This suggests that there is no dependence of the mobility on the intensity in the range of illumination studied [34].