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To cite this article: D Kudryashov et al 2016 J. Phys.: Conf. Ser. 741 012013

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The temperature dependence of the electrical conductivity in Cu₂O thin films grown by magnetron sputtering

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Abstract. The temperature dependence of the electrical conductivity in Cu₂O thin films grown by magnetron sputtering at room temperature under different rf-power was investigated. Calculated activation energy of the conductivity for copper oxide (I) films linearly increases with increase in sputtering power reflecting an increasing in concentration of gap states.

1. Introduction

A growing interest in oxide photovoltaics is caused by the low cost, non-toxicity of many metal oxides and scalability at the industrial scale. Due to developing of modern growth technique it is possible to manufacturing oxide solar cells under ambient conditions. Copper oxide (I) is one of the most interesting material in terms of photovoltaic because it is a direct-gap p-type semiconductor with a band gap of 2.2 eV and a high optical absorption coefficient [1]. Numerical simulations of Cu₂O-based solar cell (SC) performance limit show about 12% efficiency [2]. However, the state of the art of recent values for the efficiency of these SC does not exceed 5.38% [3]. The main reason is the low quality of the oxide layer and its interfaces. For poor quality p-type amorphous Cu₂O thin films due to a large concentration of gap states the Fermi level (indicated by the activation energy E_A of the layer) will be close to midgap position. Otherwise the Fermi level will be located near valence band. Its position can be estimated from the measurements of dark conductivity (σ) as a function of temperature [4]:

$$\sigma_{dark}(T) = \sigma_0 \exp\left(-E_A / kT\right) \tag{1}$$

The aim of this work is to investigate the temperature dependence of the electrical conductivity in Cu₂O thin films grown by magnetron sputtering under different conditions.

2. Experimental

Deposition of Cu₂O thin films was carried out using rf magnetron sputtering setup (Boc Edwards Auto 500RF). Cu_2O films with thickness of 150 nm were deposited on Si(100) and glass substrates at different rf-power at room temperature. Pure argon (99.999 %) was used as working gas. Control of the oxide layers thickness was carried out using a profilometer Ambios XP-1. SEM images were

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Saint Petersburg OPEN 2016	
Journal of Physics: Conference Series 741 (2016) 012013	3

analyzed using a scanning electron microscope SEM (Zeiss SUPRA 25). XRD spectra were measured using PANalytical X'Pert PRO equipment. Electrical conductivity measurements were carried out with Keithley 2400 and thermo stabilized holder under temperature range of 13-60°C.

3. Results and discussion

SEM image of 150 nm Cu_2O thin films deposited on Si-wafer by magnetron sputtering is shown in figure 1. Cu_2O has a nano-column structure with a sharp interface between Si and copper oxide (I).



Figure 1. Cross-section SEM image of Cu₂O thin film deposited on Si-wafer under different rf-power: (a) - 80 W, (b) - 125 W, (c) - 200 W

The XRD reflex intensity measurements show nonlinear RF power dependent behavior in the range of 80-200 W (Fig. 2). It has a maximum value at the magnetron RF power of 150 W and at power of 200W demonstrates a minimal value.



Figure 2. XRD patterns of Cu₂O films (150 nm) deposited on silicon as a function of the RF power.

It should be noted that for stoichiometric and stress-free copper (I) oxide crystal the rocking curve peaks must be at 36.45 for the plane (111) and 42.33 for the plane (200) positions [5]. In our case, these maxima are shifted toward larger angular values, which may indicate a deviation from stoichiometry. Indeed, the formation of Cu_2O was conducted in an argon atmosphere without oxygen addition. A portion of oxygen atoms from Cu_2O target doesn't reach the substrate because of their high reactivity. Under these conditions the oxygen-depleted layer of copper oxide (I) is formed.

Copper (I) oxide grown on glass substrates at rf-magnetron power of 80-200W shows a transmittance of 80% for a wavelength range of 850-900 nm (Fig. 3). Based on transmittance and reflection data for

sputtered Cu₂O thin films an absorption spectra was calculated (Fig. 4a). It can be seen that increase in magnetron sputtering power leads to decrease of copper (I) oxide absorption edge (Fig 4b).



Figure 3. Transmission spectra of rf-magnetron sputtered Cu₂O thin film (150 nm) deposited on glass as a function of the RF power.



Figure 4. Absorption spectra (a) and a plot of $(\alpha h\nu)^2$ vs. photon energy (b) for Cu₂O thin films deposited on glass as a function of the RF power.

Current-Voltage characteristic curves measured at different temperatures for Cu_2O thin films deposited on glass substrate are shown in figure 5a. All I-V curves exhibit a linear relationship between the applied voltage and the resulting electric current. Arrhenius plot of conductivity is shown in figure 5b where the slope reflects an activation energy for p-type Cu_2O .



Figure 5(a,b). (a) IV curves and (b) fitting for Cu₂O thin film deposited at 50 W.

An activation energy values for Cu_2O thin films grown at different sputtering powers at room temperature are shown in figure 6.



Figure 6. An activation energy of deposited Cu₂O films as a function of the rf-power.

An activation energy of copper oxide (I) films linearly increases with increase in sputtering power. The shift of the Fermi level toward mid gap is associated with increased density of gap states due to the rise of the defect concentration with rf power. Similar behavior was found in [6] where it was shown that increasing of sputtering power results in changing of copper oxide (I) films morphology.

4. Conclusions

The temperature dependence of the electrical conductivity in Cu_2O thin films grown by magnetron sputtering under different rf-power was investigated. Calculated activation energy of copper oxide (I) films linearly increases with increasing of sputtering power reflecting an increasing in concentration of gap states.

Acknowledgment

The reported study was partially supported by RFBR research project № 15-08-06645A

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