Electrical and optical properties of ZnO, CuO thin films and fabrication of (ZnO/CuO) heterojunction solar cell by thermal treatment

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Abstract: Electrical properties (carrier concentration, mobility, resistivity) of zinc oxide thin films deposited on glass substrates by (LPCVD) has been studied. Thermal annealing in air showed that ideal annealing temperature is about 250°C. Films of copper oxide (CuO) and (CuO/ZnO) solar cell were prepared by vacuum deposition of copper films followed by thermal annealing. Structural properties of the CuO films and I-V characteristics were studied upon thermal annealing and showed that a photosensitive (ZnO/CuO) heterojunction may be obtained by thermal treatment temperature about 500°C.

Keywords: Cuprous oxide, spatial atmospheric ALD, ZnO/Cu₂O heterojunction, solar cell

1. Introduction
Solar cells (SC) based on oxide heterostructures have long remained outside the area of scientific interest on the part of researchers. However, at present time, a slowdown in the efficiency growth of both silicon and AlGaAs semiconductor-based efficiency has become clearly visible, and the search for new materials for SC has begun actively. One of these materials is copper oxide – CuO. Being a straight-band semiconductor with a band gap of 2.2 eV, copper oxide also has a high absorption coefficient [1] and is characterized by p-type conductivity. In combination with a wide-band semiconductor, such as zinc oxide. It is possible to form a ZnO/ CuO heterojunction, which can be used to produce a solar cell with a theoretically achievable efficiency value of about 20% [2]. At the moment, an efficiency value of 4.1% has already been achieved for a ZnO/ CuO heterojunction-based SC [3]. ZnO has unique properties for instance a wide band gap of ~3.37 eV [4], high exciton binding energy (~60MeV) [5], effective ultraviolet photoluminescence, high optical transparency in the visible range more than (80%) [6], and high electrical conductivity. Currently, zinc oxide is used to create various sensors and detectors, piezoelectric devices, as a transparent conducting contact in solar panels and other devices [7]. The growing interest in zinc oxide-based heterojunctions is associated with wide opportunities for practical applications. In particular, a p-n transition based on n-ZnO and p-CuO is promising, so methods for obtaining ZnO/CuO hetero-junctions are actively developing [8,9,12]. In this paper, the properties of ZnO films deposited by the LPCVD method and (ZnO/CuO) structures are studied by spraying the copper film onto the substrate followed by thermal annealing treatment to improve the I – V characteristics.
2. Experimental

Zinc oxide films were obtained by low pressure chemical vapor deposition (LPCVD). Diethylcinc \(((\text{C}_2\text{H}_5)_2\text{Zn})\), or DEZ, and deionized water were used as precursors, the concentration ratio was \(\frac{H_2O}{\text{DEZ}} = \frac{5}{6}\), a gas mixture of 2\% \(\text{B}_2\text{H}_6\) in hydrogen was used for doping ZnO films with boron. The process was optimized sequentially by optimizing the temperature and pressure, and then by optimizing the gas flow ratio. Pulsed light annealing treatment of \((\text{ZnO/CuO})\) structures was obtained in an installation containing 6 halogen lamps with a power of 1 kW for (60sec). The wavelength region (800-1100 nm) is \(\sim 80\%\), then gradually decreases to \(\sim 60\%\) at 600 nm and drops to zero in the self-absorption region of \(\sim 370\) nm. In this case, the optical transmission spectrum shows optical interference in the film in the wavelength range of 600-1100 nm, which indicates a high uniformity of the film thickness. The electrical parameters of ZnO films were determined by measuring the resistivity and carrier concentration using the Hall effect at room temperature using a four-probe method in the van der Pau configuration on an HMS-3000 (Ecopia) installation with a 0.55 T magnetostatic magnet. To study the electrical properties of ZnO films on glass substrates, they were cut into square samples with dimensions of 10×10 mm. Measurements of the electrical properties of a set of ZnO samples cut from a single substrate showed a very small variation of electrical parameters in the initial samples within 5\%.

3. Results and discussion

The parameters of the initial ZnO samples Were: electron concentration n~\(1\times10^{20}\) cm\(^{-3}\), carrier mobility 30 cm\(^2\)/V. s, resistivity \(2\times10^{-3}\) Ω.cm, sheet resistance \(\sim 12\) Ohms. The effect of thermal processing in the temperature range from \(200^\circ\text{C}-500^\circ\text{C}\) is studied on the sheet resistance of ZnO. It is found that the sheet resistance of ZnO films do not change until the annealing temperature is \(200^\circ\text{C}\), then in the temperature range from 250°C to 500°C, the resistance of the films increases, apparently, annealing in air reduces the concentration of oxygen vacancies and causes growth the concentration of adsorbed oxygen at the grain boundaries, which leads, first, to the capture of free carriers at the grain boundaries and, accordingly, causes a depletion of the volume. Second, the appearance of a charge at the grain boundaries leads to strong scattering of free carriers, see Figure 1.

![Figure 1. Dependence of sheet resistance of the ZnO film on the annealing temperature.](image-url)
In order to obtain opaque electrical and optical characteristics of ZnO films, it is necessary to avoid long-term treatments at high temperature, see, (Figures 2 and 3). To obtain (ZnO/CuO) structures, thin copper films were sprayed on the substrate surface by magnetron sputtering at a pressure of 10⁻⁵ bar. To control the optical properties, clean glass substrates were attached next to the ZnO samples. After deposition, the films of CuO and the structures (ZnO/CuO) were annealed to improve the electrical properties and I-V characteristics. Figure 4. shows x-ray Images of copper thin films deposited on ZnO substrates and annealed at various temperatures (220 °C -500 °C) in air. After annealing at 220 °C, an intense diffraction peak appears at 2θ=36.6 which can be attributed to (111) reflection of the Cu₂O cubic phase. At higher temperatures, this reflex becomes less intense, while the peaks at angles 2θ =35-40°, which correspond to the reflexes (110), (002), (111) the monoclinic phase of CuO becomes more intense. Thus, x-ray diffraction results correlate with optical absorption data. From these results, it can be concluded that
annealing of copper films at 220 °C -550 °C, leads to form a mixed phase of (CuO-Cu$_2$O), while the contribution of the phases depends on the temperature and time annealing, see (Figures 4 and 5).

![Figure 4](image.png)

**Figure 4.** Composition and structure of copper thin films obtained by thermal oxidation of copper.

The I-V characteristics of (ZnO/CuO) structures obtained by deposition of copper thin films on the surface of ZnO layers, improve volt-ampere characteristics were formed during thermal annealing of copper films at 200-500°C. It was observed that the I-V characteristics of (ZnO/CuO) of the samples depend on the time of thermal annealing and temperature. The initial structure which obtained before annealing showed that the I-V characteristics were close to ohmic, and a weak asymmetry of forward and reverse characteristics was observed. This may indicate a critical role for the tunnel current [11]. However, we were observed after thermal annealing treatment in the range (200 °C -500 °C) leads to decrease in leakage currents and an increase in the value of the potential barrier. This indicates a significant contribution of tunnelling processes through surface by structural defects [10,11] and allows us to improve I-V characteristics as Figure 6 showed.

![Figure 5](image.png)

**Figure 5.** Changes in thin films thickness depending on the annealing time.
The solar cell structures (ZnO/ CuO) obtained after thermal annealing at temperature of (500˚C) show a typical I-V characteristic when the forward current increases. The dominance of multi-stage tunnelling and recombination processes through traps in the (ZnO/ CuO) structure is evidenced by the literature data on temperature dependences of the volt-ampere characteristics \[10\]. The process of tunnelling through a thin layer of bulk charge is also significant, so to reduce the non-ideal factors and suppress tunnelling leakage currents, a layer of high-resistance ZnO is created at the border of the hetero-structure \[11\]. Thus, short annealing times and temperature annealing improved the electrical and optical properties of ZnO and allow obtaining (n-ZnO/p-CuO) heterojunctions.

4. Conclusions
The effect of thermal treatment on the electrical and optical properties of ZnO films obtained by the PLCVD method is investigated. Annealing of ZnO films at temperatures above 200 ˚C causes degradation of electrical properties, the carrier concentration and mobility decrease, and the sheet resistance increases. Subsequent annealing of the samples in air leads to a significant restoration of the electrical parameters. It is established that the method of deposition of thin layers of copper on ZnO films with subsequent rapid oxidation in air for 60 sec. At temperature ranged (250 ˚C -500 ˚C), a photosensitive thin-film ZnO/ CuO heterojunction was obtained.

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