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CHARACTERIZATION OF LOW COST P-CU_2O/N-CUO JUNCTION

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Abstract
Optical and electrical properties of thin film p-Cu_2O/n-CuO junction were investigated. It was found that such junction can be fabricated by controlled oxidation of copper films in 400-500 ^oC in different O_2 and Ar partial pressures. Clear diode characteristics were observed at room temperature (25 ^oC) for the thin film device fabricated on transparent conductive glass substrates. The breakdown voltage and threshold voltages were -0.95 V and 0.75 V, respectively. Optical properties of Cu_2O and CuO thin films clearly indicated that each film and their junction well agree with previously reported data.

***Keywords**: p-n junctions, CuO, Cu_2O, thin films.*

1. Introduction

Copper forms two different oxides such as cuprous oxide (Cu_2O) and cupric oxide (CuO). Cu_2O is a p-type semiconductor and has a bandgap of 2.1 eV. CuO is an n-type semiconductor with bandgap of 1.21-1.51 eV. Cu_2O is a brown yellowish material and CuO is a black color material. It is known that CuO is more thermally stable materials and thus oxidation of Cu_2O produces CuO. Both Cu_2O and CuO have been investigated for gas sensor applications [1], catalysts [2] as well as photocells [3]. CuO is a low coast material. Thin films of CuO have been prepared using spray pyrolysis [4] and electrochemical [5] methods. Thin films of Cu_2O have been fabricated using the reactive sputtering methods [1, 3], molecular beam epitaxy [6], chemical vapor deposition [7] and reactive rf magnetron sputtering [8]. The CuO is typically prepared by chemical methods and high temperature oxidation of copper. It is easy to form CuO than Cu_2O because of the stability of CuO with high oxidation number.

It is very rare to have the same elemental oxides in both p-type and n-type forms. However, junction characteristics of p-Cu_2O/n-CuO have not been reported. Within this paper, junction characteristics of these two forms of copper oxides are presented. Both Cu_2O and CuO thin films were formed by oxidation of copper thin films under controlled conditions. The structure and optical properties were investigated for individual films. Then a p-n junction was made using these two films by appropriate selection of oxidation steps. Optical and electrical properties of these junctions were also investigated.

2. Experimental

Copper films were coated by thermal evaporation in a high vacuum system ($<10^{-7}$ Torr) on commercially available conductive (ITO) and amorphous glass substrates in order to measure electrical and structural properties, respectively. The distance between the tantalum filament and the substrates was 15 cm. Longer separation between the filament and substrate results a uniform coating of film. CuO films were fabricated by oxidizing 100-150nm thick Cu films at 500 ^oC for 20 minutes in air. The heating process was carried out in a quartz tube furnace in atmospheric pressure. Then a second copper layer of 100-150nm thick was deposited on this CuO film using thermal evaporation in vacuum. Subsequently, the film was annealed at 400 ^oC for 6 minutes in 10%O_2 and 90%Ar in order to prepare Cu_2O layer. In this process, the top Cu layer was converted to Cu_2O. Argon gas was passed immediately after the Cu_2O was formed. This was observed using optical reflectance technique. When the oxidation process was completed, the reflection of light beam was drastically reduced. Passing 100% Ar through the system and immediate reduction of temperature prevented further oxidation of the film. In order to make ohmic contact to Cu_2O film, a thin copper film and Au film were coated subsequently by vacuum evaporation. When the copper back contact was fabricated, copper wires were cleaned with acetic acid to remove any surface oxide of copper. These copper wires were immediately introduced into the system and evacuated the system to 10^{-7} Torr. These extra precautions were taken to avoid any cupric oxide film formation on Cu_2O layer. Schematic diagram of final diode structure is shown in Fig. 1.

The structure and surface properties were measured by the X-ray diffraction (XRD, Cu-Kα) and atomic force microscopy (AFM). Optical properties were measured by a double beam spectrophotometer. The current-voltage (I-V) characteristics were measured with a computerized electrometer (Keithly 236 source measurement unit).

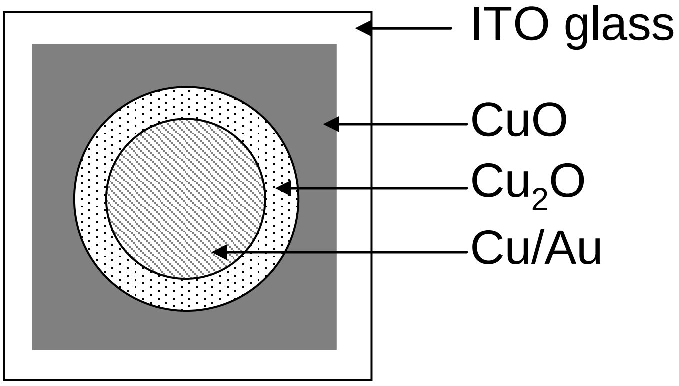

Figure 1. Schematic of p-Cu_2O/n-CuO junction fabricated on a ITO glass substrate.

3. Results and Discussion

3.1. Structure and optical properties of copper oxide films

The structure of individual CuO and Cu_2O oxide films prepared on amorphous glass substrates were investigated with XRD measurements as shown in Fig. 2. The CuO films synthesized at conditions given in experimental part exhibited XRD peaks corresponding to (111) and (112) planes. The Cu_2O films fabricated at conditions given in experimental part indicated a strong peak corresponding to (111) plane. In CuO films, no any other peak was appeared. In the case of Cu_2O film, very low intensity peaks can be seen corresponding to CuO structure.

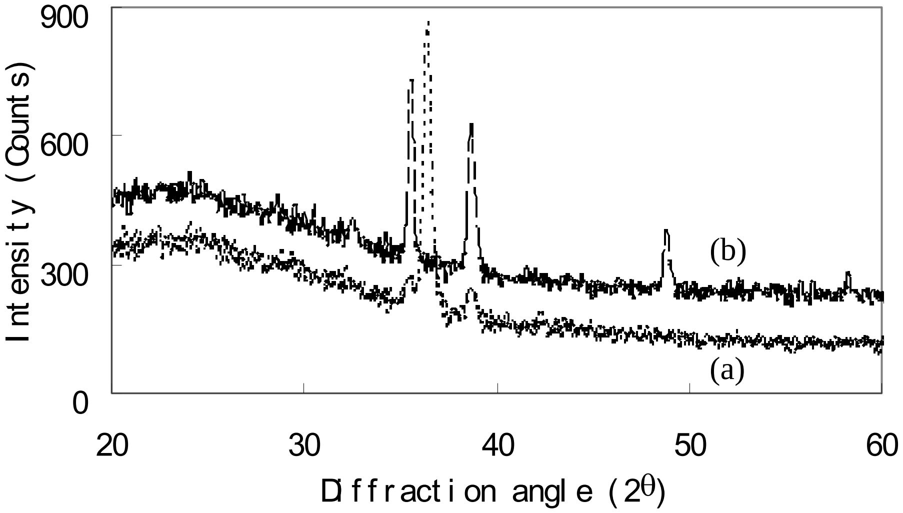

Figure 2. XRD patterns of (a) Cu_2O and (b) CuO films coated on glass substrates

This small signal can be attributed to the exposure of surface layer of Cu_2O film into the atmosphere and continuous oxidation during the heating process. These results clearly indicate that fabrication of Cu_2O/CuO junction is possible by making a CuO films by heating at high temperature and making a Cu_2O film by heating at low temperature in 10% O_2.

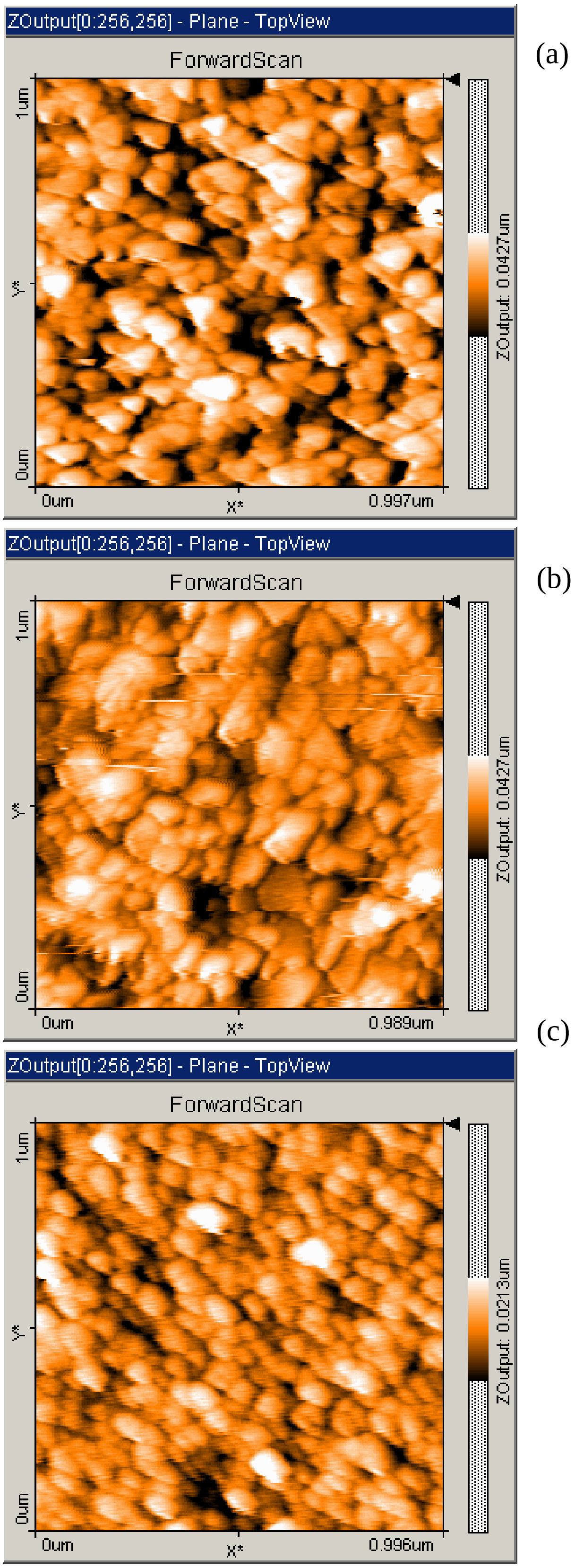

Figure 3. AFM images of (a) Cu_2O film on glass (b) CuO film on glass and (c) CuO film on ITO

Figure 3 shows the AFM images of CuO and Cu_2O prepared on amorphous glass substrates along with CuO prepared on conductive glass substrates. The surface of both CuO and Cu_2O films are somewhat similar. According to Fig.3 (a) and (b), the CuO film is denser than Cu_2O film. This can be attributed to the expansion of copper crystallites during heating process and filling the space in Cu_2O film. The AFM image of CuO film coated on conductive glass substrate indicated densely packed and uniform size crystallites. This morphology can be influenced by ITO which has small grain like structure.

Figure 4 shows the optical transmittance of CuO and Cu_2O films coated on amorphous glass substrates measured with a double beam spectrophotometer. It can be seen that the Cu_2O films has a absorption edge around 590 nm corresponding to the bandgap of 2.1 eV. However, the CuO films indicated optical absorption for a wide rage of wavelengths. It is known that CuO has a wide range of band gaps in 1-21-1.51eV corresponding to 1025-820 nm. The strong absorption in this range of wavelength can be seen in the spectrums shown in Fig.4. The Optical transmittance of Cu_2O/CuO is also shown in Fig.4 (curve-c). In this film, a strong absorption can be seen for the absorption corresponding to the CuO films.

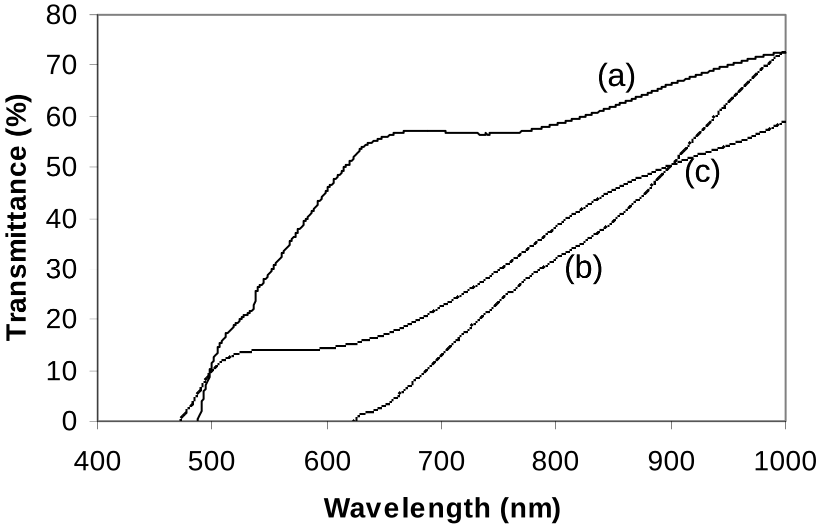

Figure 4. Optical transmittance spectra of (a) Cu_2O film, (b) CuO film and (c) Cu_2O/CuO layers coated on glass substrate.

3.2. Electrical Properties

Electrical properties of Cu_2O and CuO films were measured as shown in Fig. 5. The both films were made on conductive glass substrates and the back contacts were made using evaporated thin copper layer and gold layer. Fig.5 (a) and (b) indicate that both Cu_2O and CuO have ohmic contact with ITO and Cu contacts.

Figure 5 (c) indicates the current-voltage (I-V) characteristics of p-Cu_2O/n-CuO junction. It clearly indicated characteristics of typical diode. In the forward bias direction, a threshold voltage of 0.8 V was observed and the current density was increased after this voltage. In the reverse bias direction, the junction breakdown could be observed at 0.95 V. At this breakdown voltage, the current was suddenly increased as predicted in an ideal diode case. However, after the current pass to a level of 0.0175 mA/cm^2, the device shows an ohmic characteristic. After device breakdown, it indicated ohmic contact throughout the voltage range as shown in Fig.5 (d). This phenomenon can be described as the conversion of Cu_2O into CuO by thermally induced oxidation in the some regions of Cu_2O. The I-V

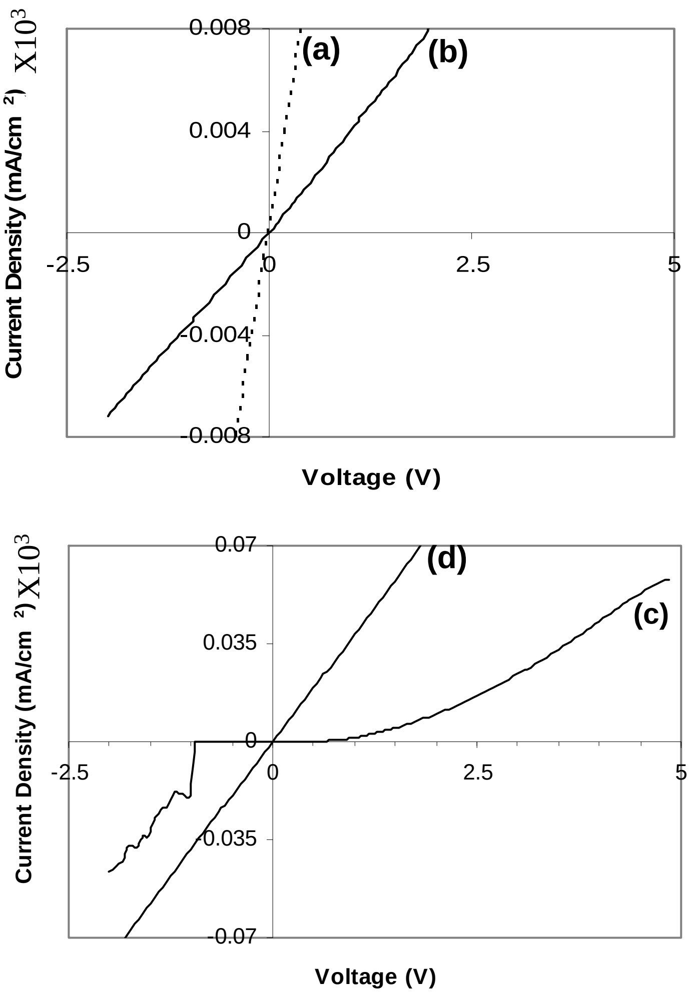

Figure 5. Current-Voltage (I-V) characteristic of copper oxide films: Upper (a) ITO/Cu_2O/Cu-gold, (b) ITO/CuO/Cu-gold, (c) p-Cu_2O/n-CuO (d) I-V characteristics after breakdown.

curve after breakdown process [line (d)] clearly shows the same gradient as CuO film. The property of this device is very interesting because after breakdown the device it converts to ohmic level rather than gaining high current densities as in other diodes. This process is not similar to typical Si or Ge based diode structures, After the breakdown happened, a drastic increase of current has been predicted. However, in the present device, conversion of less stable materials (Cu_2O) to more stable material (CuO) results limitation of breakdown current levels of the device.

4. Conclusion

Thin films of CuO and Cu_2O were successfully formed by vacuum evaporation and heating method on glass substrates and ITO substrates. By adjusting the heating temperature and ambient conditions, two layer devices could be fabricated. The electronic properties of p-Cu_2O/n-CuO junction reveal that device has diode characteristics. But after breakdown, the device converted to a resistor. The breakdown voltage and threshold voltage were -0.95 V and 0.75 V, respectively. This investigation will lead to developments of copper oxide based junction devices which can be used in solar energy conversion and other electronic device fabrication.

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