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Observation of defect interface states at the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ junction using thermally stimulated I-V measurements

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Abstract

A simple method was developed to fabricate a $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ p-n junction diode and I-V characteristics of the diode was measured at various temperatures. It was revealed that there are current transport mechanisms at the junction which are leading to high leakage currents. Namely, an oscillatory behaviour of the current with the temperature was observed under reverse bias conditions. This behaviour was interpreted as the thermally enhanced tunnelling at the junction due to the existence of defect interface states. We believe that proper surface treatment might reduce the density of interface states, and thereby improve the I-V characteristics of the diode.

1. INTRODUCTION

Studies on current-voltage (I-V) characteristics of various semiconductor heterojunctions have been a subject over the last few decades because their promising applications in various devices^{1,2}. Among the early semiconducting materials, Cu_2O had attracted much attention because the low-cost of preparation and possible application in solar energy converting devices^{3,4}. However, all the reported data were only based on the thermally grown p-type Cu_2O . Recently it has been shown that n-type conductivity is possible in Cu_2O films prepared by the electrodeposition technique⁵. In our investigation we have used the n-type Cu_2O films to fabricate a p-n junction diode with p-type Cu_xS . Our investigation reveals that the general diode-characteristics are possible with the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ heterojunction though there are complicate current transport

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mechanisms at the junction. Particularly, we have observed a thermally stimulated current carrying mechanism at the reverse bias of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode.

2. EXPERIMENTAL

Thin Cu_2O films were deposited on the copper substrates by using the technique described earlier⁵. Copper plates were initially polished with a sand paper and then washed, degreased and rinsed in distilled water. Then the electrodeposition was carried out in an aqueous electrolyte containing 0.1 M cupric acetate for 30 min. The samples were rinsed with distilled water and etched with an aqueous KCNS solution for 1 s followed by the rinsing in distilled water. The p-n junction was fabricated by passing a mixture of nitrogen gas and ammonium sulphide over the Cu_2O surface. Hence we could form a very thin layer of Cu_xS on top of Cu_2O film. The thickness of Cu_xS can easily be controlled by the rate of flow of the gas mixture, time of exposure and the temperature of the substrate. It was also observed that the good reproducibility as well as the reasonably good diode characteristics can be obtained by preparing the samples at 75°C .

The schematic representation of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode is given in Fig 1. The front contact to the diode was made by mechanically pressing a platinum plate to the front Cu_xS surface while the back contact was made to the copper substrate. The diode was kept inside an electrical oven and the temperature was monitored using a thermocouple while measuring the I-V characteristics of the diode. I-V characteristics were obtained with a Keithley Model 197 digital multimeter and Farnell Model D 30 2 power supply. We have repeated these experiments for a commercial germanium diode in order to compare the results of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode with the germanium diode.

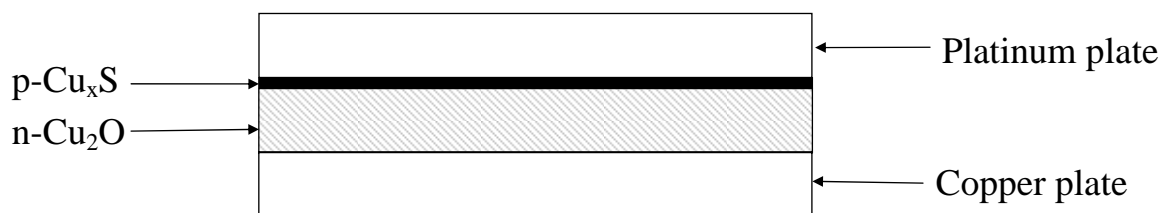


Fig. 1 Schematic diagram of the p- $\text{Cu}_x\text{S}/\text{n-Cu}_2\text{O}$ diode

3. RESULTS AND DISCUSSION

The typical I-V characteristics of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode at various temperatures is shown in Fig 2. The voltage range was limited to ± 300 mV because it was observed that at higher voltages the junction is destroyed. For comparison, we have shown in the inset

of Fig 2 the I-V characteristics of a commercial germanium diode. As it can be clearly seen, the basic diode characteristics are evident in the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode compared with the germanium diode. However, the reverse current is larger in the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode. This is not surprising because the diode that we have made here is a junction between two polycrystalline materials of Cu_2O and Cu_xS , whereas the junction of germanium diode is the homojunction of good quality materials.



Fig. 2 I-V characteristics of the p- $\text{Cu}_x\text{S}/\text{n-Cu}_2\text{O}$ diode at different temperatures (Inset shows I-V characteristics of a germanium diode)

The important observation, in our opinion, is that the reverse current of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode shows some cross-over effect which is not seen in germanium diode. Fig 3 shows this behaviour clearly. This is more evident, as shown in Fig 4, if the voltage is kept constant while scanning the temperature. The oscillatory behaviour of the current variation with temperature at higher reverse bias condition is somewhat peculiar and suggests that thermally enhanced transport mechanism at the interface will be responsible for this observation.

In general, the junction that we are dealing here is not a perfect or not even a nearly perfect one. As mentioned earlier the materials involved are polycrystalline and therefore the current transport mechanisms are not simple thermal emission and

tunnelling but a complicate process. The general I-V behaviour of the $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode follows the germanium diode and therefore the additional features appearing at the reverse bias must be due to an additional current transport mechanism at the interface. This can be explained with a simple model with the existence of defect electronic states at the interface as shown in Fig 5.



Fig. 3 Reverse current of the p- $\text{Cu}_x\text{S}/\text{n-Cu}_2\text{O}$ diode at various temperatures

Tunnelling would be a possible explanation for the observed temperature dependence of the reverse current. Indeed, the tunnelling current is influenced by the density and the distribution of the defect states at the interface⁶. These states are occupied or unoccupied according to the bias voltage. Also, thermal emission of these states are very significant in determining the availability of density of states for tunnelling and thereby the tunnelling current. Therefore, we can expect that, depending on the location of the defect states, the reverse current is modified at some temperature values. Indeed, this is what we have observed in Fig 4. At this stage we are not in a position to find the exact location of the defect states but our experimental observation suggests the existence of such defect states. We believe that, by removing the interface states with proper surface treatments at the fabricating stage, the diode characteristics can be improved significantly. Therefore, our simple experimental procedure demonstrate the possibility of observing interface states by the simple I-V measurement technique.



Fig. 4 The variation of reverse current of the p-Cu_xS/n-Cu₂O diode with temperature at different constant applied voltages

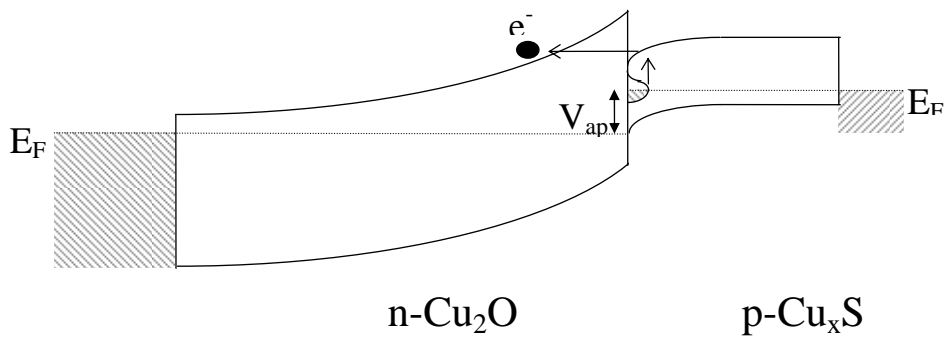


Fig. 5 Schematic representation of the band diagram of the Cu₂O/Cu_xS interface. Electrons from the occupied states are excited to the conduction band of the Cu_xS and then tunnel to the conduction band of the Cu₂O

4. CONCLUSION

In conclusion, we have demonstrated a simple experimental technique that can be used to fabricate a $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ p-n junction diode. In general, the diode characteristics of $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ diode follows the commercial germanium diode characteristics with an exception of a larger reverse current. Further, thermally stimulated change in occupancy of carriers in the defect interface states seems to facilitate the current transport mechanisms at the junction leading to high reverse current at elevated temperatures.

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