DC Bias Dependent Impedance Spectroscopic Study of Polycrystalline Copper Oxide Thin Films

Eheta Samul Kadir\textsuperscript{a)} and Rabindra Nath Gayen\textsuperscript{b)}

\textit{Department of Physics, 86/1, College Street, Presidency University, Kolkata-700073}
\textsuperscript{a)Corresponding author: eheta.rs@presiuniv.ac.in}
\textsuperscript{b)rabin.physics@presiuniv.ac.in}

Abstract- Here we report the effect of grain-boundaries on the charge transport in polycrystalline copper oxide (CuO) thin films by dc bias dependent impedance spectroscopic study at room temperature. The films are synthesized by easy and cost-effective sol-gel spin coating technique. X-ray diffraction pattern confirms the formation of CuO which is polycrystalline by nature. The optical band gap of the film as estimated from the transmittance spectrum is \(\sim 2.60\) eV. Room temperature dc bias dependent complex impedance spectroscopic studies indicate the effect of core grain and grain boundaries on the transport properties of CuO thin films. An electrical circuit model comprised of two parallel RC circuits in series is used to find out relaxation time (\(\tau\)) distributions in polycrystalline film arising out of different electrical responses of grains and grain boundaries. As the grain-boundary contribution in electrical transport is significantly small, the film exhibits very good photo response under solar spectrum making it suitable for photovoltaic applications.

1. INTRODUCTION

Metal oxide semiconductors (MOS) have been receiving great attention since last few decades as one of the most promising components of electronic and optoelectronic devices like thin film transistors\textsuperscript{1}, energy storage and conversion devices\textsuperscript{2} and sensors\textsuperscript{3}. Among various metal oxide semiconductors, two oxides of copper, cuprous oxide (Cu\(_2\)O) and cupric oxide or simply copper oxide (CuO) have garnered special interest because of their p-type conductivity, suitable electrical and optical properties, non-toxicity, easy processing and chemical stability which propel their application in numerous technological devices\textsuperscript{4-6}. Polycrystalline CuO thin films with p-type conductivity and optical band gap of 2.0 eV offer a unique opportunity to realize all-oxide based heterojunctions for electronic and optoelectronic applications. But the major problem with polycrystalline CuO thin film arises out of poor transportation of charge carriers inside the film due to the presence of large number of grain boundaries of nanocrystalline grains. The grain boundary induced potential barrier significantly affect the charge carrier mobility of polycrystalline films which limits their application possibilities. Thus, to fabricate good quality film with better transport remains a challenge to the researchers. Also, it is immensely important to understand the effect of grain boundaries on the charge transport phenomena of polycrystalline thin films for their usefulness in device application. Among various fabrication methods\textsuperscript{7-9}, sol-gel spin coating technique is easy, low-cost, environment friendly and scalable method to obtain good quality CuO thin films.

On the other hand, complex impedance spectroscopic studies provide significant insights of the different electrical processes inside a polycrystalline material. Under the application of small ac signal, different regions like core grains, grain boundaries and interfaces response differently for various frequency range which is apparent from the obtained distribution of relaxation times. Conventionally, different electrical circuit model is fitted with experimentally obtained real part of impedance (\(Z'\)) vs. imaginary part of impedance (\(Z''\)) data by trial to find out relaxation times corresponding to different electrical regions like grains or grain boundaries. But, the impedance spectra measured under different dc bias voltage can confirm the grain boundary contribution for a chosen circuit model as the relaxation time would exhibit significant variation with external bias contrary to that of the grain contribution\textsuperscript{10}. Here, we have presented the dc bias dependent impedance spectroscopic studies of CuO
polycrystalline thin film synthesized by sol-gel spin coating method to confirm the effect of grain boundaries on the charge transport.

2. EXPERIMENTAL DETAILS

To prepare the solution, 0.5M(2.49gm) of copper acetate was dissolved into 25 ml of isopropanol. Few drops of DEA were added into the mixture to maintain transparency of the solution. Finally, few drops of acetic acid were poured into the mixture as stabilizer. Now this compound mixture was stirred in a beaker using magnetic stirrer for 1 hour at an intermediate temperature of 60°C. After that the solution was stirred for another 1 day at room temperature in order to obtain homogeneous mixture. Finally, this solution was filtered through filter paper to eliminate precipitated compounds to get transparent solution.

To deposit CuO thin film on glass or FTO (Fluorine doped tin oxide)-coated glass substrate spin coating technique was used. The prepared solution was spin coated on the substrates for 30 seconds at a constant speed of 3000 rpm using a programmable spin coater. Then the coating was dried in an air oven at 120°C for 10 mins. This spin coating and drying processes were repeated six times to get uniform film with desired thickness. Finally, the film was annealed at 400°C for 1 hour to remove unwanted compounds. This yielded pure nanostructured thin film of CuO.

3. RESULTS AND DISCUSSIONS

The X-ray diffraction pattern of the synthesized CuO thin film is shown in fig. 1. The polycrystalline nature of the film is apparent from the XRD pattern with multiple diffraction peaks of monoclinic crystal structure of CuO (JCPDS card no. 45-0937). The average crystallite size has been estimated from the Scherrer relation as follows

\[ D_{hkl} = \frac{k\lambda}{\beta_{hkl} \cos \theta} \]  

(1)

Where, \(D_{hkl}\) is the average crystallite size, \(k\) is called crystalline shape factor which is taken 0.9 here considering spherical grains, \(\lambda\) is the wavelength of incident x-ray which is 0.154 nm here, \(\beta_{hkl}\) is the full width at half maxima (FWHM) of the XRD peak arising out of (hkl) planes and \(\theta\) is the peak position. The average value of crystallite size of CuO appears to be \(\sim 33\) nm.

![Figure 1](image)

**FIGURE 1.** XRD pattern of CuO thin film

Optical properties of the developed CuO film is studied by transmission spectrum using UV-Vis spectrometer at room temperature. Figure 2(a) shows the transmittance spectrum of CuO thin film which indicates enhanced absorption in the visible range of electromagnetic spectrum. From this transmission spectra absorption coefficient is determined by using the relation

\[ \alpha = \frac{1}{d \ln (1/T)} \]  

(2)

Where \(d\) is the thickness of the film and \(T\) is the transmittance. Optical absorption coefficient of semiconductor as function of energy of incident radiation is[12]

\[ \alpha = (A/hv) \times (hv - E_g)^n \]  

(3)
Where $\alpha$ is the absorption coefficient and $hv$ is the photon energy. $A$ is a constant depends on nature of transition whether it is direct or indirect. $m$ is a constant appears to be 0.5 for direct band gap semiconductor. The functional relationship between $(\alpha hv)^2$ and photon energy is represented in fig. 2(b). Band gap of the nanocomposite is determined by extrapolating the linear portion of the curve to $(\alpha hv)^2 = 0$. Band gap value calculated by this method turns out to be 2.64 eV at room temperature.

![Transmittance spectrum of CuO thin film](image1)

**FIGURE 2.** (a) Transmittance spectrum of CuO thin film, (b) $hv$ vs. $(\alpha hv)^2$ plot to estimate the optical band gap of CuO thin film

Impedance spectroscopic measurement is carried out at room temperature in the frequency range of 50Hz-5MHz to explore conduction mechanism of the polycrystalline thin film. From fig. 2(a) it is found that that impedance falls with increase in frequency. Impedance of the nanocomposite turns out to be few tens of kiloohm at lower frequency range. But beyond a certain frequency a rapid fall occurs in the impedance which reduces to a fixed value at high frequency region. This can be attributed due to existence of capacitive nature in the nanocomposite. There can various reasons of emergence of capacitive effects inside the nanocomposites like due to accumulation of charge particles at grain, grain boundaries, electrode interfaces and defect sites. But main reason for emergence of capacitive effect is due clogging of charge particles at inter-grain boundaries. This is known as formation of Schottky barrier between relatively high conducting grain and low conducting interfaces. At low frequency charge particles transfer between grains overcoming the high potential barrier is responsible for emergence of high impedance. But at high frequency potential barrier becomes less effective due to which impedance falls. Also, at high frequency impedance becomes frequency independent due to the fact that at high frequency polarization phenomena due to grain boundary becomes ineffective. Also, there is a fall in impedance is observed with increasing external bias voltage. Usually the impedance is a measure of resistance offered to charge particles at the interfaces. With increment in bias voltage interfacial polarization also enhances which in turn rises capacitive effect. Higher the dc bias voltage, more charges are able to overcome the potential barrier which results in less charge accumulation at the interface and less resistance is offered which consequently reduces impedance.

Complex impedance can be presented as

$$Z = Z' + jZ''$$

Figure 3(b) depicts Nyquist plot (real part of complex impedance vs imaginary part of complex impedance) obtained from experimentally measured impedance spectroscopy data for CuO nanocomposite with variation of external bias voltage. Arcs of the semi-circles of the Nyquist plots have a decreasing tendency with higher applied external bias voltage due fall in complex impedance. In order to acquire information about conduction mechanism in composite due to effects of grain, host – filler interface, electrodes and imperfections, obtained Nyquist plot has been fitted by electrical model circuit consisting of a series resistance and two parallel R – C circuits. Resistances and capacitances of this modeled circuit are founded from EIS spectrum analyzing software. Using these parameters, we calculated relaxation times $\tau_1 = R_1C_1$ and $\tau_2 = R_2C_2$ represents electrical responses emerging from cores at high frequency and interfaces at low frequency respectively. Figure 3(d) depicts variation of different time constants arising from contributions of only grains and interfaces as they performs major role in relaxation phenomena.
\( \tau_2 \) appears to be relatively higher compared to \( \tau_1 \) because interface induced polarization is comparatively higher than polarization induced in core. It has been observed that relatively no variation occurs in \( \tau_1 \) with external bias voltage which is assumed to be contribution arriving from core grains. External bias voltage does not induce any further polarization to grains. But \( \tau_2 \) which is considered to be relaxation contribution from grain boundaries or interfaces varies significantly with external bias voltage. Moreover \( \tau_2 \) has a decaying nature with application of external bias voltage. This is so because with application of higher external bias voltage less accumulation of charge particles occurs at the interfaces which in turn reduces capacitive nature and hence time constant for the interfaces.

**FIGURE 3.** plot obtained from impedance spectra at various bias voltages, (c) Fitting of Nyquist plot for a model circuit shown in inset (d) Variation of \( \tau_1 \) and \( \tau_2 \) with applied dc bias voltage

Figure 4 evidently displays the response of CuO thin film when exposed to light similar to solar spectrum. Now being a direct band gap semiconductor having a band gap nearly 2.64 eV a significant portion of the spectrum generates electron hole pair which can be converted into usable electrical energy. When a dc bias voltage is applied across the thin film a small current flows across it even if the light is off which is known as dark current. But as soon as light is turned on current gradually starts to rise and then slowly saturates. This excess current generated in presence of light is known as photocurrent. Here we have set the dark current to zero as reference. The figure clearly indicates that there is almost 20µA rise in current in presence of light.
Response time is always an important parameter for any light conversion device. Sharp response time is heavily desirable for any photo conversion devices. The time by which photocurrent rises to 90% of its maximum or saturation value is often called time constant. For CuO nanocrystalline thin film this time constant arises out to be 3.15 sec which is considered to be short response time.

![FIGURE 4 photoresponse of CuO thin film](image)

CONCLUSION

Polycrystalline CuO thin films were synthesised by sol-gel spin coating technique. Microstructural studies confirmed the formation of polycrystalline CuO thin films with monoclinic crystal system which comprised of nanocrystallites of average grain size ~ 33nm. The optical band gap as estimated from the transmittance spectrum of the film was ~ 2.64 eV. The room temperature impedance spectra, measured in the frequency range 50Hz-5MHz, were fitted into an electrical circuit model comprised of two parallel RC circuit connected in series. The time constants (τ=RC) of parallel circuit represented the relaxation time of electrical responses from core grain and grain boundaries of the polycrystalline CuO films. The relaxation time for grain boundaries showed more variation with applied small dc bias voltage compared to that of grain contribution. The very small value of relaxation time confirmed the good quality films with better transport. The CuO film showed good photoresponse behaviour with response time ~ 3.15s under solar spectrum illumination.

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