Influence of Laser Pulse Energy on The Electrical Properties of Cu$_2$O Nanoparticles Prepared by Laser Induce Plasma

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Abstract. In this work, copper oxide films (Cu$_2$O) were grown using laser ablation from Nd:YAG laser with a wavelength of 1064 nm in vacuum. Electrical properties of the nanoparticles were investigated as a function of the laser pulse energies, including (600 - 900) mJ and annealing temperature was varied at (473, 573 and 673)K. Hall Effect measurement was used to determine the electrical mobility, carrier concentration, conductivity and majority of electrical carriers.

Keywords: Thin films, Pulsed laser deposition, Cu$_2$O, Electric Properties, Nanoparticles

1. Introduction

Pulsed laser deposition (PLD) ranks as one of the most successful technique, due to its high controllability, relatively modest costs, and flexibility [1]. Laser ablation has been used to grow thin films of many deferent materials in the process commonly referred to as pulsed laser deposition (PLD). Congruent evaporation inherent to PLD, maintaining the stoichiometry of a multi element target in the growing thin film, has led to considerable success in the manufacture of high-Tc superconducting thin films [2].

Copper oxide is a promising non-toxic and low cost semiconductor with potential applications in photovoltaic devices and sensor applications [3, 4]. There are two stable copper oxide phases according to oxygen composition. One is cupric oxide (CuO) which has a monoclinic phase; the other one is cuprous oxide (Cu$_2$O) and has a cubic phase [5, 6]. Due to copper oxides potential applications, such as, in solar cells [7], catalysis [8], and magnetic devices [9], much attention has been attracted.

The Hall Effect is used to investigate the behavior of charge transport in metal and semiconductor substrates when a combination of a magnetic field and an electric field called Lorenz force is applied to the substrate in a perpendicular direction. Additionally, Hall Effect measurement can be used to distinguish whether the type of semiconductor is n-type or p-type [10]. The magnetic field and the charge q provide the force on a particle which can be mentioned as the cross product of velocity and magnetic field those are perpendicular to the force vector as shown in equation 1[10].

\[ \vec{F} = (q \vec{v}) \times (\vec{B}) \]  

Equation 1 shows that the Lorenz force \( \vec{F} \) relies on the charge of the particle \( q \), and the velocity of the particle \( \vec{v} \) due to the presence of an Electric field \( \vec{E} \) and a magnetic field \( \vec{B} \).[10]
\[ \vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) \]  \hspace{1cm} (2)

Where, \( \vec{F} \) is Lorenz force
\( q \) is electric charge of particle (1.602x10^{-19} \text{ C})
\( \vec{E} \) is electric field
\( \vec{v} \) is velocity of the particle
\( \vec{B} \) is magnetic field

When a magnetic field and a constant current source applied are known, Hall voltage can be calculated by using equation 3[10]

\[ V_H = \frac{IB}{qnd} \]  \hspace{1cm} (3)

Where, \( I \) = current
\( B \) = magnetic field
\( d \) = sample thickness
\( q \) = electric charge of a particle

On the other hand, the multiplication of \( n \) and \( d \) can be mentioned as \( n_L \) (layer density). Therefore,[10]

\[ n_L = \frac{IB}{q/V_H} \]  \hspace{1cm} (4)

From the above equation \( n_L \), layer density of charge carriers of a semiconductor can be calculated by using the measured Hall voltage \( V_H \) and given values of \( I, B \) and \( q \).

Moreover, Hall mobility can be calculated using the sheet resistance value,[10]

\[ \mu = \frac{V_H}{R_sB} \]  \hspace{1cm} (5)

Where, \( \mu \) = Hall mobility, \( R_s \)=sheet resistance.

In this work for the first time, the effect changing the laser energy and annealing temperature on the electrical properties of the prepared Cu_{2}O NPs thin films were investigated by Hall Effect and active energy measurement.

2. Experimental
The target of the deposition was copper oxide of 99.7% purity where a sample was taken and measured weighing up to (2g) and was pressed by the hydraulic piston and gets the material in tablet where the target is bombed by PLD. The PLD periment was carried out under vacuum pressure of \((10^{-3} \text{ mbar by using Varian DS219 Rotary pump}) \) for this pressure's sufficiency to oxidize product Cu_{2}O. The beam of Nd:YAG laser with fundamental harmonic frequency \((\lambda = 1064 \text{ nm, 10 ns, 6 Hz})\) was focused onto Cu_{2}O target with quartz lens \((f = 10 \text{ cm})\). The substrate distance from the target was glass. The PLD experiment was performed at room temperature and the as grown samples were annealed after deposition. PLD setup scheme has been shown in Figuer1. All Cu_{2}O films were deposited on glass microscope slides which were cleaned well with ultrasonic path. The Cu_{2}O target was ablated by 500 pulses. The laser pulse energy was varied in the range \((600-900) \text{ mJ} \) with increment 100 mJ in each step. Finally, the Cu_{2}O thin film the resistivity of Cu_{2}O films is measured by DC measurements after depositing metal electrodes (Al) on the samples using appropriate masks. The method comprises a temperature controller oven. The films glass samples are heated in the oven from room temperature up to 150°C with step of 10°C by using the electrical circuit, Electrical resistance is then measured directly for all steps with digital electrometer and Measurement of hall effect of Cu_{2}O film where Type of Hall Measurement System is Ecopia HMS-3000.
3. Results and discussion

Hall Effect measurement was used to determine the electrical mobility, carrier concentration, conductivity and majority of electrical carrier's type for thin films at different annealing temperatures and at different energy pulse laser.

Table 1 show's that all films were p-type.. This result has a good agreement with [11]. The carrier mobility increases with increase of annealing temperatures to 300K, 473K and 573K. Then, conductivity increases with increase of annealing temperatures to 300 K, 473K. It was found that the conductivity at 573K is high, due to the change of mixed phase (CuO and Cu2O), as the material behaved previously in [11]. while the carrier concentration is small in the stable state and increases in status mix phase. The carrier mobility, conductivity and carrier concentration increased with increasing the laser pulse energy as shown in table 1 below. Where electrical properties have been improved effect by annealing. This result has a good agreement with[15].

Table 1. Hall measurements for thin film Cu2O at different annealing temperature and different energy pulse laser

| Sample     | \(\sigma_{RT} (\Omega^{-1}.cm^{-1})\) | \(R_H (\Omega) \times 10^6\) | \(n (cm^{-3}) \times 10^{12}\) | \(\mu_H (cm^2/v.s)\) |
|------------|-------------------------------------|----------------------------|----------------------------|-------------------|
| RT         | 2.148*10^{-3}                       | 2.865                      | 2.18                       | 61.55             |
| Annealing  |                                     |                            |                            |                   |
| 473 K      | 9.340*10^{-3}                       | 1.360                      | 4.5                        | 1.27*10^{3}       |
| 573 K      | 2.390*10^{-2}                       | 1.309                      | 4.77                       | 3.130*10^{5}      |
| 673 K      | 1.192*10^{-3}                       | 6.66                       | 0.93                       | 7.94*10^{5}       |
| Energy of plus laser | 600mj 2.102*10^{-5} | 195                        | 0.0032                     | 0.4101            |
|            | 700mj 2.294*10^{-5}                 | 67.30                      | 0.0092                     | 15.1              |
|            | 800mj 2.32*10^{-5}                  | 9.399                      | 0.066                      | 218.1             |
|            | 900mj 1.192*10^{-4}                 | 6.669                      | 0.093                      | 794.7             |

Figure 2 illustrates the relationship between resistivity with inverse laser pulse energy.
Figure 2. Variation of Ln (σ) with temperature for Cu₂O films deposited at various energy pulse laser
Through the figure, we observe that the relation between variation of Ln (σ) and annealing temperature is proportional for Cu₂O thin films. Except for sample at 573K that shows similar behavior to carrier concentration due to phase mixing.

Figure 3. Variation of Ln (σ) with temperature for Cu₂O films with different annealing temperature
From Hall Effect measurements, when increasing the laser energy, both the conductivity and number of charge carriers increase due to the change in energy gap Resulting from a phase change due to increased laser energy and heat as behaved in paper [14] Figure 4 illustrates the relationship between activation energy with inverse laser pulse energy. We observe a decrease in the activation energy while increasing the laser energy, which improves the electrical properties of Cu₂O thin film.
Figure 4. Variation of DC activation energies for thin films with different energy pulse laser.

Figure 5 illustrates the relationship between activation energy with different annealing temperature, we observe a decrease in activation energy while increasing the annealing temperature. But, at 573 K the behavior changes inversely because of the mixed phase as shown in [12], which has a low activation energy. This goes in a good agreement with the previous reports of Jundale et al [13], where increasing annealing temperature increasing activation energy.

**Table 2.** DC activation energies, their ranges and conductivity at room temperature for different energy pulse laser.

| Laser energy (mJ) | $E_a1$ (eV) | Range (K) | $E_a2$ (eV) | Range (K) | $\sigma_{RT}$ ($\Omega^{-1}\text{cm}^{-1}$) |
|-------------------|-------------|-----------|-------------|-----------|-------------------|
| 600               | 0.335       | 293-343   | 0.505       | 343-423   | 4.43E-06          |
5. Effects the resistivity from 47.57 to 8.30E-05 their electrical properties through rapid thermal annealing. Phase copper oxide films have mixed phase of CuO and Cu$_2$O. The Hall Effect studies confirmed that all the deposited films were p-type in nature. Low resistivity ($\rho$) $0.418 \times 10^2 \Omega$ cm is reported for the mixed phase copper oxide film deposited at 573K. Where the characteristics of Cu$_2$O films improved their electrical properties through rapid thermal annealing changing the pulse laser energy effects the resistivity from 47.57 $10^3 \Omega$ cm to 8.3 $10^3 \Omega$ cm.

### Table 3. DC activation energies, their ranges and conductivity at room temperature for different annealing temperature

| T (K) | $E_{a1}$ (eV) | Range (K) | $E_{a2}$ (eV) | Range (K) | $\sigma_{RT}$ ($\Omega^{-1} \text{cm}^{-1}$) |
|-------|----------------|-----------|---------------|-----------|-----------------------------------------------|
| RT    | 0.271          | 293-343   | 0.391         | 343-423   | 8.30E-05                                      |
| 473   | 0.260          | 293-343   | 0.361         | 343-423   | 2.38E-04                                      |
| 573   | 0.258          | 293-343   | 0.342         | 343-423   | 5.39E-03                                      |
| 673   | 0.297          | 293-343   | 0.423         | 343-423   | 1.68E-03                                      |

4. Conclusion

In this work Copper oxide thin films have been successfully deposited by pulse laser technique on the glass substrate with different temperatures and different energy pulse laser. When annealing at 473K has cuprous oxide (Cu$_2$O) phase whereas the films annealing at 573 have mixed phase of CuO and Cu$_2$O. The Hall Effect studies confirmed that all the deposited films were p-type in nature. Low resistivity ($\rho$) $0.418 \times 10^2 \Omega$ cm is reported for the mixed phase copper oxide film deposited at 573K. Where the characteristics of Cu$_2$O films improved their electrical properties through rapid thermal annealing changing the pulse laser energy effects the resistivity from 47.57 $10^3 \Omega$ cm to 8.3 $10^3 \Omega$ cm.

5. References

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