Effect of Laser Pulse Energy on the Optical Properties of Cu_2O Films by Pulsed Laser Deposition

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In this work copper oxide films (Cu_2O) were grown by pulsed laser deposition. The films were analyzed by X-ray diffraction and their thickness by using profilometer while the UV-VIS absorption spectra were recorded by using UV-VIS spectrometer. Pulsed Nd:YAG laser was used with varying its pulse energy, with distance between target and substrate 1 cm, and substrate temperature at room temperature, vacuum pressure was fixed at 6×10^{-2} mbar, number of pulses = 1000. The optical properties of as-grown film like energy gap has been measured experimentally and the effects of laser pulse energy on it were studied. There is linear relation between energy gap and pulse energy. The specific energy gap of Cu_2O film can be controlled by changing laser pulse energy and fixing other pulsed laser deposition parameter such as substrate temperature, distance between target and substrate, background pressure and number of pulses.

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1. Introduction

During the past decades pulsed laser ablation has evolved into a powerful method of thin film deposition. After its early success in the context of the deposition of high temperature superconductor films, this technique has been applied for obtaining thin films of other materials such as ferrites, ferroelectrics, diamond-like carbon, etc. [1]. Pulsed laser deposition (PLD) ranks as one of the most successful technique, due to its high controllability, relatively modest costs, and flexibility [2]. Laser ablation has been used to grow thin films of many different materials in the process commonly referred to as pulsed laser deposition (PLD). Congruent evaporation inherent to PLD, maintaining the stoichiometry of a multielement target in the growing thin film, has led to considerable success in the manufacture of high-T_c superconducting thin films [3].

In our view, this method offers several distinct advantages over the conventional methods of metal films deposition especially in the context of the realization of metallic multilayers and superlattices. These are as follows.
(i) Contrary to the conventional methods used to fabricate metallic multilayers, the laser ablation method does not require ultrahigh vacuum conditions.
(ii) No equilibrium global heating of target occurs. This is useful to suppress spurious degassing and contamination.
(iii) By rapid refluxing of the ambient gases, deposition of metal/oxide multilayers should also be possible.
(iv) The laser ablation route offers higher film adhesion because the impinging radicals on the surface are energetic.
(v) The ablation thresholds of oxides (fraction of a J/cm^2) are much lower as compared to the thresholds in the case of metals (few J/cm^2) [1].

However, PLD suffers from two disadvantages not evident with other thin film growth techniques, which have inhibited the full utilization of PLD in the manufacture of single element thin films and multilayers. These are as follows.
(i) The emission of macroscopic molten globules from the irradiated target which are deposited as particulates onto the substrate along with the growing atomic thin film.
(ii) A highly forward directed flux of atomic material leaving the target surface, normally attributed to collisions amongst emitted particles which leads to the formation of a thermalization region, or the Knudsen layer. Collisions have the effect of changing the particle velocity distribution from that emitted, a consequence of which is forward peaking of the polar distribution [3]. In recent years, copper oxide thin films have attracted much interest due to their potential applications for solar cells and gas sensor. Cuprous oxide (Cu_2O) and cupric oxide (CuO) are the two main semiconductor phases of copper oxide with narrow band gap [4]. Cu_2O is a *p*-type semiconductor of cubic structure with a direct band gap of 2.1–2.6 eV [5, 6]. Its outstanding excitonic properties including a large exciton binding energy (≈140 MeV) have been the target of much fundamental research during the past decades. Cu_2O layers on semiconductor and insulator substrates have interesting properties for alternative photovoltaic devices and photoelectrodes in high-efficiency photoelectrochemical cells and different techniques have been explored to fabricate Cu_2O layers with device quality electronic properties [5]. Cu_2O has high theoretical solar cell efficiency, is available in abundance, and makes the process simple. Studies on its application to solar cells have been carried out since the 1970s; however, the practical application of Cu_2O to solar cells is limited because of the difficulty in improving

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the electrical properties [7, 8]. During the past few years, Cu_2O, one of the representative of transparent metal oxide (TMOs) has been widely investigated due to its potential applications in gas sensors, capacitors and memory devices and high-T_c superconductors. It was also reported that Cu_2O films show large optical nonlinearities, which may be a potential candidate for optical computing and related application [9, 10]. Aiping Chen et al. (2009) studied the influence of substrate temperature and oxygen pressure on the structural and optical properties of CuO and Cu_2O [4].

In this work we study the effects of the laser energy parameter on the optical properties of the Cu_2O films prepared by PLD technique on glass substrate and choosing the appropriate Cu_2O energy gap for the various industrial usages like solar cell, sensors, etc.

2. Experimental

The target of the deposition was Cu bulk with purity 99.999%, shaped like disc with a diameter of 3 cm and the target surface was smoothed by using coarse glass paper. PLD experiment was carried out under vacuum pressure (6×10^{-2} mbar by using Varian DS219 Rotary pump) for this pressure's sufficiency to oxidize pure Cu and product Cu_2O. The beam of Nd:YAG laser with fundamental harmonic frequency ($\lambda = 1064$ nm, 10 ns, 6 Hz) was focused onto Cu target with quartz lens ($f = 10$ cm), the target was kept onto rotating holder (speed 4 rev/min) to prevent fast drilling. The substrate distance from the target was fixed to 1 cm. The PLD experiment was performed at room temperature and the as-grown samples were not annealed after deposition. PLD setup scheme has been shown in Fig. 1. Optical properties (UV/VIS absorption spectrum) of the Cu_2O films were performed using Cary 100 Conc. (UV-Visible spectrometer). All Cu_2O films were deposited on glass microscope slides which were cleaned well with ultrasonic path. The Cu target was ablated by 1000 pulses (time of deposition = 2.77 min). The laser pulse energy was varied in the range 200–1000 mJ with increment 200 mJ in each step. Finally, the Cu_2O thin film thickness was measured by using Black-CXR-SR-25 Ellipsometer (50 A–20 μm range).

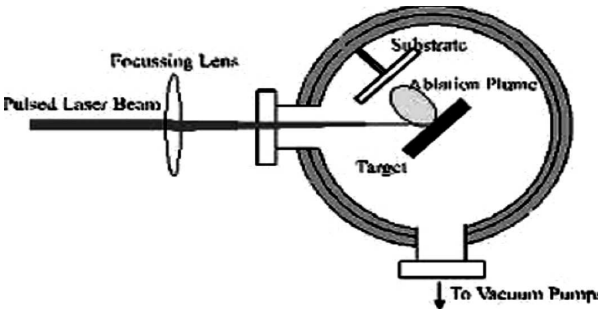

Fig. 1. Schematic diagram of the PLD experimental setup.

3. Results and discussion

In Fig. 2, the identity of Cu_2O has been approved by measuring XRD and comparing it with the standard XRD of Cu_2O using the program Match 1.11, it is found that the intensity peak is at $2\theta = 42.52°$ with the Miller indices (020), the resultant film has amorphous nature because there is no substrate temperature nor as-deposit annealing temperature since the sample has been grown in room temperature only.

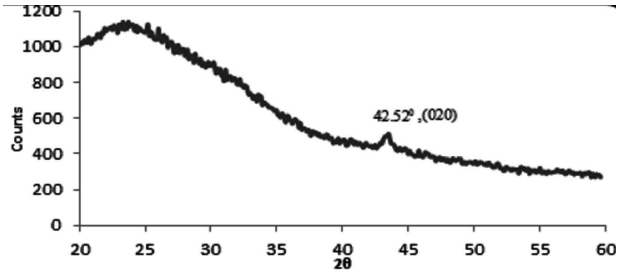

Fig. 2. XRD of Cu_2O at $P = 6{\times}10^{-2}$ mbar, $D = 1$ cm, Nd:YAG laser at $\lambda = 1064$ nm, $T_s = RT$, $N_{pulse} = 1000$, $E_p = 1000$ mJ.

Absorption spectrum of Cu_2O, at $P = 6 \times 10^{-2}$ mbar,$D_{T-S} = 1$ cm,using Nd:YAG laser at $\lambda = 1064$ nm, and room temperature $T_s = 27\,°C$, no. of pulses = 1000, varying laser pulse energy within 200, 400, 600, 800, 1000 mJ, has been shown in Fig. 3. It shows that the UV-VIS absorption of Cu_2O depends strongly on the laser pulse energy (E_p).

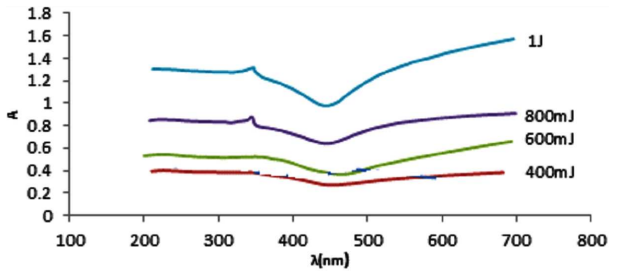

Fig. 3. Absorbance spectra of Cu_2O at $P = 6 \times 10^{-2}$ mbar, $D = 1$ cm, Nd:YAG laser at $\lambda = 1064$ nm, $T_s = RT$, $N_{pulse} = 1000$, $E_p = 1000$ mJ.

It is found that the absorption A increased as E_p increased due to the increment in ablation atoms from the target which deposit on the substrate as a thin film, i.e. increasing Cu_2O thickness and as a result the absorbance increases according to the following relation $A_b = \alpha t/2.303$ where A_b is the absorbance, t is the film thickness and α is the absorption coefficient. Also due to the higher laser energy which can supply more kinetic energy to the materials ejected during the deposition process. As the laser energy increases, the increase in the adatom mobility on the substrate surface could provide the conditions necessary for smaller and denser nc-Cu_2O. The band gap energy E_g of Cu_2O of a direct band gap is calculated from

$$\left(\frac{\alpha h\nu}{A}\right)^2 = h\nu - E_g, \tag{1}$$

where α is the absorption coefficient, h — the Planck constant, ν — the frequency of the incident photon, A — constant, so α^2 is plotted as a function of the photon energy $h\nu$ which gives a linear relation and by using linear fitting the band gap energy can be found.

Figure 4 shows the variation of $(\alpha h\nu)^2$ as a function of photon energy to extract the value of E_g as a function of E_p.

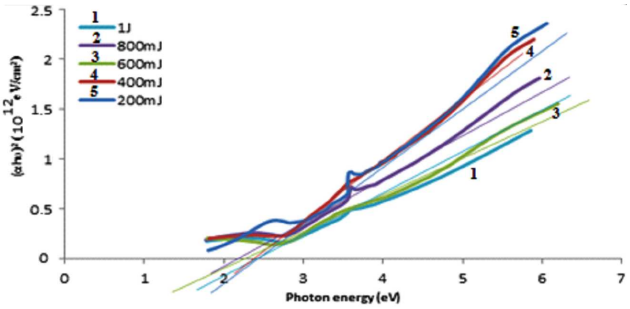

Fig. 4. Variation of $(\alpha h\nu)^2$ as a function of photon energy.

It is clear that as laser pulse energy increases, the energy gap E_p and thin film thickness t increase linearly, too, as shown in Figs. 5 and 6, respectively.

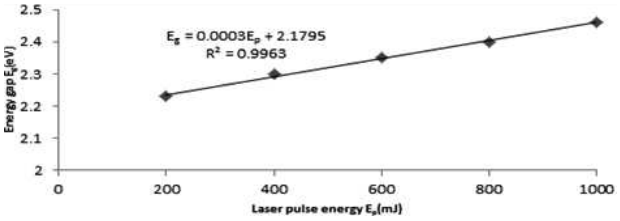

Fig. 5. The relationship between energy gap and laser pulse energy at $D = 1$ cm, $P = 6 \times 10^{-2}$ mbar.

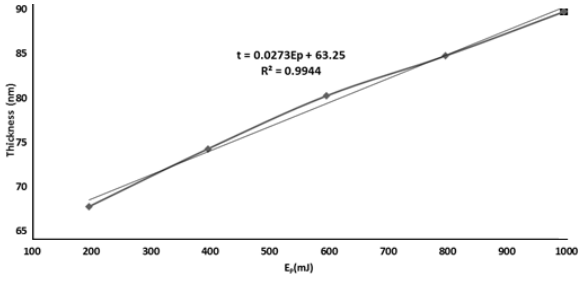

Fig. 6. The relationship between CuO_2 thin film thickness and laser pulse energy at $D = 1$ cm, $P = 6 \times 10^{-2}$ mbar.

This is due to increase of the kinetic energy of the ablated atoms from the Cu target because of the high laser pulse energy. By increasing the laser pulse energy the absorbance of the thin film increases, hence, from Eq. (1) the energy gap increases as the thin film absorbance increases so finally, as the laser energy pulse increases, the absorbance of thin film increases as a result of increase of its thickness and results in the increase of the energy gap. By linear fitting of the data, energy gap E_g of Cu_2O can be controlled by choosing a specific laser pulse energy E_p according to the linear fitting equation

$$E_g = 0.0003E_p + 2.1795 \tag{2}$$

with $R^2 = 0.9963$, where R^2 is a measure of goodness of fit. The experimental E_g in Eq. (2) consists in theoretical E_g of Cu_2O (2–2.6) with error percent ≈4–9%. For example if we want to get $E_g = 2.6$ eV for Cu_2O, nearly 1.4 J pulse energy must be delivered to the Cu target under the same aforementioned conditions $P_b = 6 \times 10^{-2}$ mbar, $D = 1$ cm, $T_s = RT$, $N_{pulse} = 1000$. The output energy gap agrees with theoretical energy gap. It is found that as laser pulse energy increases the band gap energy of Cu_2O increases linearly. The fitting equation of Cu_2O thin film thickness versus pulse laser energy is obtained from

$$t = 0.0273E_p + 63.25 \tag{3}$$

with $R^2 = 0.9963$. Figure 7 shows the inversely proportional relationship between the lattice parameter of Cu_2O as a function of its thickness.

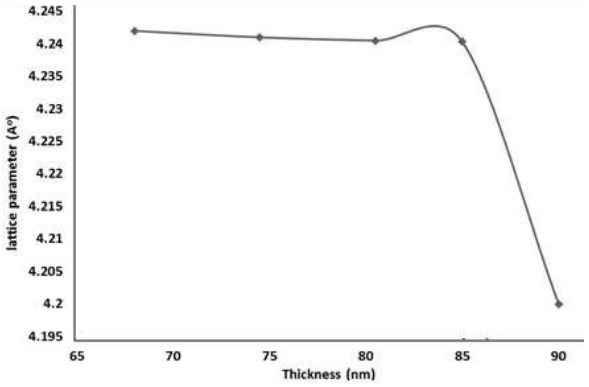

Fig. 7. The relationship between CuO_2 thin film lattice parameter and its thickness at $D = 1$ cm, $P = 6 \times 10^{-2}$ mbar.

As the thickness increases the lattice parameter decreases because of (i) negative lattice mismatch between substrate and Cu_2O thin film, (ii) high density of Cu_2O vacancies that cause to decrease the lattice parameter.

4. Conclusions

The effect of laser pulse energy E_p on the band gap energy was discussed. UV-VIS absorption results indicate that suitable energy gap of Cu_2O can be obtained by adjusting the laser pulse energy at fixing other parameters like substrate temperature, vacuum pressure, distance between target and substrate. As laser energy pulse increases, the absorbance of thin film increases and as a result the energy gap will increase which leads to increase and this may be due to improving the crystallite size and decreasing the transmittance. The optimum

value of energy gap E_g depends on the right choosing of laser pulse energy E_p.

However, it is plausible to argue that the energy gap or absorbance varied due to a lattice constant widening or narrowing.

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