Optical Properties of Copper Oxide Thin Film synthesized by SILAR Method

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Abstract: In the present work copper chloride dehydrate and hot distilled water was used as cation and anion precursor solutions for synthesizing copper oxide thin film by SILAR technique. To study the structural properties in detail, these samples were characterized by X-ray Diffraction (XRD). The size of the particles was calculated from the XRD spectra with the help of Scherrer formula. It was found 2.33 nm and among various structures of copper oxide, the monoclinic structure is observed. The SEM images showed spherical morphology for the as prepared sample. The optical properties of the film were studied by using UV-VIS absorption spectrum. Tauc plot was plotted and band gap energy was determined. All these results are discussed in this paper.

Keywords: Copper oxide thin film, SILAR method, optical properties, band gap energy.

1. Introduction: Due to the rapid development in electronics it is necessary to create a variety of materials with required physical, electrical and optical properties so as to create modern devices. Hence scientists are paying more and more attention to tailor new and already known chemical compounds which possess the semiconductor properties. Metal oxides are the potential candidate as they are environmentally safe, non-toxic and chemically stable [1]. In addition, the elements of the metal oxides are available in earth's crust and simple; low temperature inexpensive production methods are required to obtain them [2-4].

Being industrially important material, copper oxide has been intensively studied due to its wide range of applications in various sectors like spintronics, optoelectronics, solar energy conversion, energy storage media, batteries, super capacitors, gas and biosensor technology, biomedicine, and high-temperature superconductors [5, 6]. The most common, stable, and non-toxic phases of this semiconductor are cupric oxide (CuO) and cuprous oxide (Cu_2O) [7]. CuO is a p-type semiconductor. According to various data, it possesses a monoclinic crystal lattice, a band gap of 1.2 to 2.1 eV, a high absorption coefficient (10^5 cm^{-1}, 300 K), good thermal conductivity (76.5 W mK^{-1}), and electrical resistance, (10 to 10^5 Ohm-cm) depending on the method of production [8–14]. CuO can be obtained by chemical and physical methods such as sol-gel method [15], hydrothermal methods [16], solvothermal [17], chemical precipitation [18], spray pyrolysis [8], thermal evaporation [19], magnetron sputtering [20], molecular beam epitaxy [21] etc.

In the present work, the process adopted is a modified chemical bath deposition technique known as Successive Ionic Layer Adsorption and Reaction (SILAR). It is a modified chemical bath deposition (CBD) developed by Nicolau in 1985 [22]. The method has many advantages like low cost, low process temperature, precise film-thickness control and being suitable for large-area deposition. SILAR method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with double distilled water or de-ionized water to avoid homogeneous precipitation in the solution. The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. Adsorption may be expected when two heterogeneous phases are brought into contact with each other. The SILAR is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin films of water insoluble ionic or ion covalent compounds by heterogeneous chemical reaction at the solid solution interface

between adsorbed cations, and anion. It consists of at-least four different steps: adsorption, rinsing, reaction and rinsing.

Adsorption: In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate.

Rinsing: In this step, excess adsorbed ions are rinsed away from the diffusion layer.

Rinsing: In last step of a SILAR cycle, the excess and un-reacted species and the reaction by-product from the diffusion layer are removed. If anionic precursor is water then SILAR method reduced to two steps.

Reaction: In this reaction step, the anions from anionic precursor solution are introduced to the system; this process involves the reaction of surface species with the anionic precursor.

From step 1 to step 4, a SILAR reaction cycle is completed and the thickness of the deposited film can be increased and controlled by controlling the number of reaction cycles. Since the film growth mechanism of SILAR is the layer-by-layer stacking of ions, SILAR is also called solution atomic layer deposition (SALD) or liquid atomic layer deposition (LALD).

In this work copper chloride dehydrate and hot distilled water are used as cation and anion precursor solutions to grow CuO thin films on glass substrates by the SILAR method. The deposited films were dried in air at ambient temperature. Furthermore, the films are characterized to study their morphological, structural and optical properties. These results are presented in this paper.

2. Materials and Methods

2.1 Sample Preparation:

As mentioned earlier copper chloride dehydrates and hot distilled water are used as cation and anion precursor solutions. The thin films of cupric oxide CuO have been deposited on glass slides substrates by the modified SILAR method. Initially a cationic precursor solution was made by dissolving copper chloride ($CuCl_2 \cdot 2H_2O$) in distilled water with constant stirring at room temperature. A homogeneous solution was prepared. The pH of this solution was adjusted adding the ammonia solution in it. Thus a copper-ammonia complex $[Cu(NH_3)_4]^{2+}$ was obtained for deposition of CuO thin films. For preparing the anionic solution hot distilled water was heated and kept at 80 ^oC.

The glass slides were used as substrates. Prior to use they were cleaned by boiling in chromic acid near about 5-10 min. It was followed by boiling in soap solution for 2 min. The glass substrate is cleaned by rubbing cotton; then washed with distilled water and dried in air. The as prepared glass slide substrates were immersed into $[Cu(NH_3)_4]^{2+}$ for 30 sec, then were immersed into hot distilled water (80 ^oC) for another 30 sec and dried in air for 10 sec. This completes one deposition cycle. This cycle was repeated for 30 periods. Finally the deposited films were rinsed in distilled water and dried in air at ambient temperature.

2.2 Sample Characterization:

The crystalline structures of the copper oxide thin films were examined by an X ray diffractometer (Schimadzu Lab X- 6100 at Savitribai Phule Pune University, Pune) with an incident wavelength of $\lambda = 1.54$ Å). The surface morphology of the as-prepared samples was investigated using the scanning electron microscopy measurements using a JEOL, JSM 5600 microscope at the Physics Department, SPPU, Pune. The band-gap energies of all the samples were determined from the UV–vis-spectroscopy measurements carried out at the Central Facility at Garware College, Pune.

3. Results and Discussions:

3.1. Structural and Morphological Analysis:

Fig. 1 shows the XRD pattern of CuO thin films deposited for 0.05 M concentration on glass substrate. XRD pattern shows major peaks close to 2θ equal to 33.42° and 36.92° are attributed to the (110) and (111) planes. All the diffraction patterns can be indexed to have the monoclinic crystal structure which is in good agreement with JCPDS # 800076. Crystallite size is calculated by using Scherrer's formula and found to be in the range of 2.33 nm. Lattice constants 'a' and 'c' are calculated using indexing method with an average lattice parameter a = 4.679Å and c = 5.136Å.

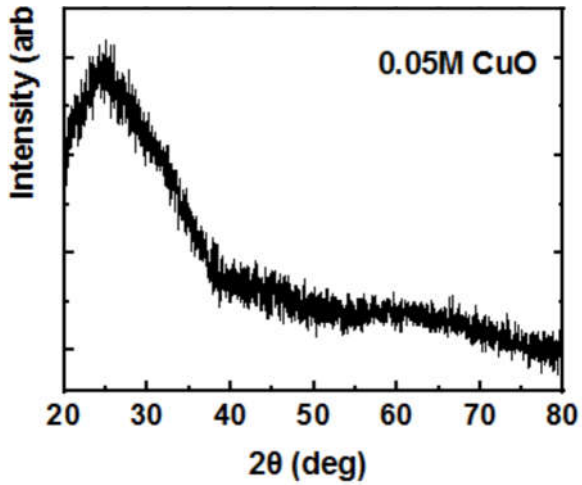

Fig. 1: XRD Spectrum of 0.05 M CuO thin film

Scanning electron microscopy (SEM) is a convenient method for studying the microstructure of thin films. The surface morphologies of the microstructure of CuO thin films for 30 cycles on glass substrate are shown in Figure 2. As shown in Figure, regular microsphere particles were observed for 0.05M CuO film.

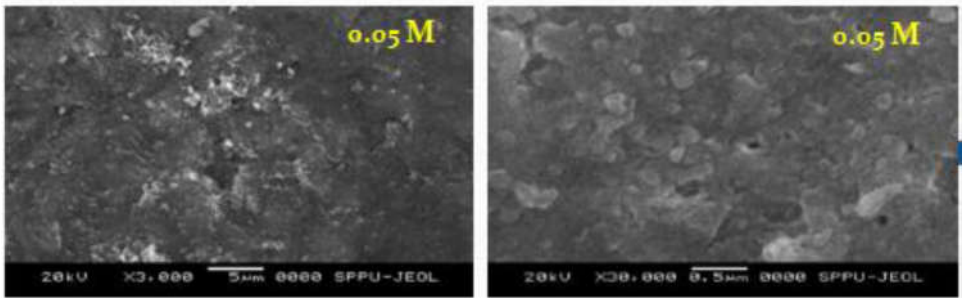

Fig. 2: SEM Image for 0.05 M CuO thin film

3.2. Optical Properties:

Fig. 3 shows the optical properties of SILAR synthesized CuO thin films for 0.05M concentration. The thin film shows a sharp absorbance peak around 370-380 nm which can be assigned to band gap of CuO.

UV-Vis absorption spectra can also be used to determine the value of the optical band gap energy and Urbach energy. Determination of the optical band gap energy can use the Tauc-plot method.

$$\alpha h\vartheta = A\,(h\vartheta - E_g)^n$$

where, $\alpha = \frac{4\pi k}{\lambda}$, here k is the absorbance value, λ is the wavelength. A is a constant indicating the sharpness (width) of the energy band side, h is Planck's constant while υ is the speed of light so h υ is photon energy (eV), then x is an indirect parameter (n = 2) and direct (n = ½). Fig. 4shows a typical Tauc plot used to estimate the direct band gap using Kubelka Munk transformation for CuO synthesized for different molarities by SILAR method. The energy band gap was found to be 2.6 eV,

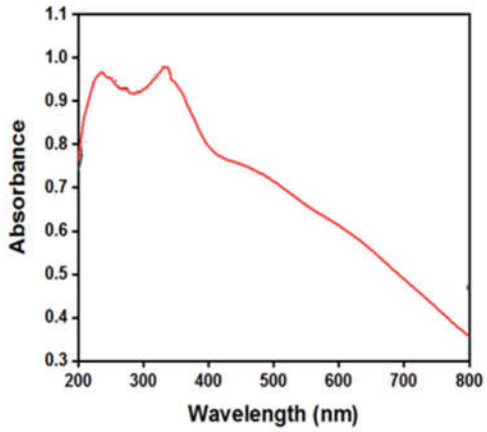

Fig. 3: UV-vis Absorption Spectrum for 0.05 M CuO thin film

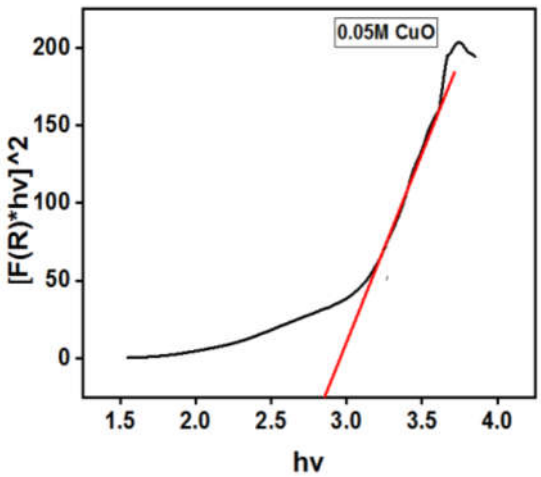

Fig. 4: Tauc Plot for 0.05 M CuO thin film

Conclusion:

CuO thin film was successfully synthesized by using SILAR Method. XRD analysis shows that the CuO film possesses monoclinic crystal structure. The SEM image of the as prepared film shows spherical morphology. Each thin film shows the sharp absorbance peak

around 370 nm which can be assigned to band gap of CuO. The band gap energy obtained from UV-Vis absorbance spectrum is found to be 2.6 eV which indicates the formation of CuO.

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