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Optical and Electrical Properties of Spin-Coated Co_3O_4 Thin Films Deposited on Glass Substrate

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Abstract: Sol–gel vacuum spin coating technique is used to prepare cobalt oxide thin film on glass substrate at a constant speed of 2000 RPM at room temperature. The samples are backed at 50˚C for two hours before annealing. The films are annealed at temperatures of 350˚C and 650˚C to investigate the effect of annealing on structural, morphological, optical and electrical properties. The samples annealed at temperature 650˚C show strong XRD diffraction peaks which indicate the spinel cubic structure of Co_3O_4. SEM study shows that the morphology of the annealed film at 650˚C becomes smooth with well oriented grains. The calculated crystallite size from XRD data is about 75 nm. It is also observed from the SEM images that the surface of the films is very rough at low temperature annealing (350˚C). The band gap of the film is calculated from optical absorption data. It is seen that the optical band gap varies with film thickness and ranges from 1.9 eV to 2.1 eV. Optical absorption measurement of the annealed film revealed that the nature of the band gap is direct. Electrical properties of the annealed film are measured using four prove technique. It is found that the electrical resistivity of the film at room temperature is 0.018 Ω–cm. The current increases with the increase of measurement temperatures which indicate the semiconducting nature of the film.

Keywords: Thin film, Co_3O_4, sol–gel technique, spin coating, XRD, SEM, optical band gap, electrical resistivity.

1 Introduction

Transition metal oxides have attracted considerable interest due to their distinctive properties in the field of electronic, optical, magnetic and catalytic [1–3]. Various methods have been used to deposit cobalt oxide film on glass substrate. Cobalt oxide prepared using sol-gel method show that it can be used to detect carbon dioxide gas [4]. It is a direct band gap p-type semiconductor having band gap in the range 1.48–2.19 eV [5]. Smooth and flat texture of cobalt thin film annealed at 700˚C is suitable for optoelectronic application [6]. Ceramic and glass industries use cobalt oxide as pigments. The solution of cobalt oxide is also used in fast drying paints and varnishes in enamel coating on steel. Cyclic-voltammetry and ganvanostatic charge-discharge methods are used to study the properties of cobalt oxide thin films for supercapacitor application [7]. The concept of light-based water splitting to convert electric energy is recent interest in the energy sector. Slow water oxidation reaction is the major problem associated with artificial photosynthesis for solar energy harvesting. Non noble cobalt oxide is a promising candidate for enhancing the water oxidation catalyst [8].

Electronic properties of spinel Co_3O_4 are investigated by many researchers using density functional theory. Their study reveals that it is a normal spinel structure which contains cobalt ions in Co^{+2} and Co^{+3} oxidation states. The ions are located at the interstitial tetrahedral (8a) and octahedral (16d) sites of fcc lattice formed by the oxygen ions [9]. Cobalt oxide has three main structures (CoO, Co_2O_3 and Co_3O_4). During high temperature annealing of as-deposited film, it crystallizes in cubic spinel structure. The crystalline phase of cobalt oxide is not easy to control. The annealing below melting point of cobalt oxide is one of the processes of phase transition. Out of three states of cobalt oxide, only two states are stable: CoO and Co_3O_4. The structures of the two oxides are cubic in nature. Electrical, electronic, photonic and optical properties of cobalt oxide have been investigated for many promising applications such as electrodes of lithium ion battery, solar selective absorber in solar cells, field emission materials and magnetic materials [10–13]. Cobalt oxide nanoparticles are also very promising materials for many magnetic supplications. It can be used as week ferromagnetism, spin canting and as superparamagnetic material [14]. The surface roughness decreases with the increase of oxidation temperature. The resistance of the Co3O4 thin film decreases with increase of annealing temperature. At lower oxidation temperature below 400˚C both the CoO and Co_3O_4 phase appear in a mixed state and disappear above 400˚C [15]. Average particle size increases at higher oxidation temperature and hence the conductivity of cobalt oxide increases. The electron or hole scattering decreases due to the grain boundary reduction [16-18].

To investigate the effect of thermal treatment on structural, morphological, optical band gap and electrical, nanocrystalline Co_3O_4 thin films have been thoroughly studied. Cobalt oxide

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thin film is prepared using low-cost sol-gel method at room temperature. Structural, morphological, optical and electrical properties are studied after annealing and the results are presented in this paper. The samples are backed at relatively low temperature before final high temperature annealing. It is observed from our study that low temperature backing of the sample affects the properties of the Co_3O_4 thin films. The main objectives of the study are to study the effect of annealing on structural, optical band gap and morphological properties of the Co_3O_4 thin films.

2. Experimental details

ACS grade cobalt acetate tetrahydrate[$(CH_3COO)_2$ $Co.4H_2O$] chemical is purchased from Sigma Aldrich and used as source materials of cobalt oxide in this research. To prepare the cobalt oxide power, 40 ml methanol is added to a few grams of cobalt acetate tetrahydrate and the mixture is stirred vigorously for one hour at a temperature of 60˚C. The color of the mixture becomes light pink. To remove hydroxide phase from pink powder and to improve the crystallinity phase, the powder sample is sintered at fixed annealed temperature and time in open air to obtain Co_3O_4. The transformation of cobalt oxyhydroxide (CoOOH) to Co_3O_4 is observed after the annealing at high temperature. After annealing at high temperature, the color of the Co_3O_4 powder becomes dark black.

Dark black powder of Co_3O_4 is added to double distilled water to make solution. The solution was placed in a magnetic stirrer and stirred for three hours at room temperature. The solution is filtered using grade-1 Whatman filter paper. Thin film of Co_3O_4 is prepared using spin coating technique from 0.02M solution. To prepare thin film of suitable size nanoparticles, 0.02M solution was used. The filtered solution is used to prepare thin films on glass substrate in a vacuum spin coater (Model: VTC-100). The glass substrate is attached to the substrate holder of the coating unit. The solution is poured on the glass substrate while the substrate is rotated at 2000RPM for 40 seconds. To remove the moisture from the as-deposited films, the sample was heated in open air at 50˚C for two hours. To improve the crystallinity and roughness of the film, the samples are annealed at 350˚C and at 650˚C for 20 minutes.

The structure of the prepared and annealed Co_3O_4 films were investigated by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE instrument. The surface morphology of the annealed Co_3O_4 films were investigated by Scanning Electron Microscopy (SEM) using a Curl Zesis (Evo-18) instrument. To determine the optical band gap of the annealed Co_3O_4 samples, optical absorption spectra of the Co_3O_4 thin films were measured by using ultraviolet visible spectroscopy (UV–VIS) in the wavelength range 400–1000 nm. A standard four probe technique is used to measure the dc electrical resistivity of Co_3O_4 thin films.

3. Results

3.1 Structural Analysis

The structure of crystalline materials can be determined from XRD measurement. X-ray diffraction patterns of Co_3O_4 thin films annealed at 650˚C is shown in Fig.1. Sharp diffraction peaks of Co_3O_4 are detected in the diffraction measurement. Diffraction peaks appear at ($2\theta \approx$ 19.012˚), ($2\theta \approx 31.295$˚), ($2\theta \approx 36.892$˚), ($2\theta \approx 38.592$˚), ($2\theta \approx 44.86$˚), ($2\theta \sim 55.69^o$), ($2\theta \approx 59.3555$) and ($2\theta \approx 65.319$˚) are corresponding to the crystallographic planes (111), (220), (311), (222), (400), (422), (511) and (440) [JCPD: 78-1970, a = 8.02˚A]. The calculations also reveal that the sample under investigation has cubic spinel structure.

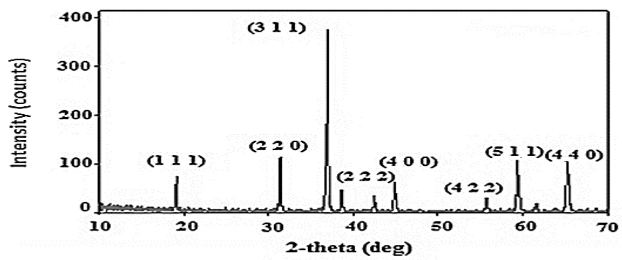

Fig. 1: XRD pattern of Co_3O_4 thin film prepared on glass substrate and annealed at 650˚C.

It is found from the structural analysis that cobalt oxide films annealed at 650˚C temperature show clear and sharp absorption peaks. It can be concluded from the above results that all the films are highly textured polycrystalline with a cubic spinel structure having a random orientation, which generally found in the growth of Co_3O_4 thin films [19-21]. The strong peak intensity found in the X-ray diffraction data indicates high crystalline structure of the Co_3O_4 [22]. The X-ray diffraction images show strong peaks of the film indicating polycrystalline nature with cubic structure having preferential orientation through (311) plane. Similar structural nature of Co_3O_4 films is observed by other researchers [23].

It is known that the orientation of atoms in the c-axis of Co_3O_4 strongly depends on the heat treatment. It is also known that the degree of orientation in the c-axis increases with annealing temperature [6, 19-21]. The crystalline size of Co_3O_4 thin films is calculated from XRD data. The average particle size of Co_3O_4 thin films are calculated from full width at half maximum of XRD strongest peaks from the Scherrer's equation, $D = C\lambda \,/\, \beta cos\theta$, where D is the mean crystallite size of the grains, C is the dimensionless shape factor whose value is close to one but is taken as 0.9 in the calculation, λ is the wavelength of X-ray, β is the width of the diffraction peak at 50 % value of maximum intensity of X-ray in radians and θ is the Bragg angle. The crystallite size of Co_3O_4 film is calculated from the strongest peak, located at (311) plane observed at $2\theta \approx$ 37˚. It is found from our measurement that the average value of the crystallite size is about 75 nm. It is also observed from the study that crystallite size increases with annealing temperature. There are many dangling bonds at the grain boundaries of cobalt-oxide thin films. These grain boundaries are reduced at higher annealing temperature and the crystallite size increases. At higher annealing temperatures, the grain boundary defects in the sample are coalescence to form larger grains. It is found from our study that the degree of structural order of Co_3O_4 films is found to improve with annealing temperatures. Study reveals that the degree of structural order of Co_3O_4 thin films is found to improve with annealing temperature [23]. At higher annealing temperature, the thermal agitation may be responsible to orient the atoms to proper equilibrium sites in the crystal structure of Co_3O_4 films. In this process the quality of nanocrystal of Co_3O_4 is enhanced.

3.2. Surface Morphological Analysis

Scanning electron microscopy is used to study the effect of annealing on the morphology of the films. The SEM image of the film annealed at 350˚C is presented in Fig. 2. Fig. 3 shows SEM image of Co_3O_4 thin film annealed 650˚C. It is seen from Fig.2 that cobalt oxide film is grown on glass substrate with many pinholes and the surface of film is partially covered with developed grains. On the other hand, it is clear from Fig. 3 that the surface of the film is well covered and became smooth at high temperature annealing. The grains grown vertically at annealing temperature of 650˚C.

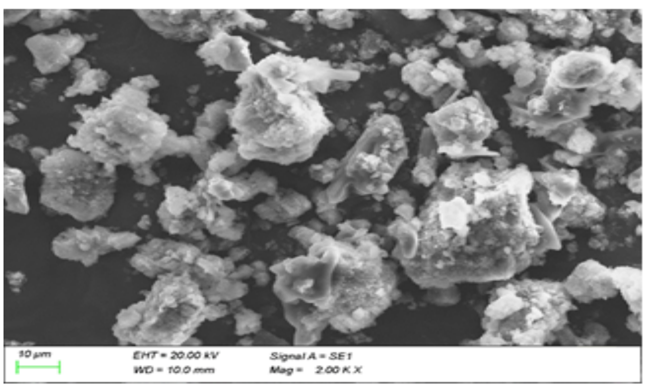

Fig. 2: SEM image of Co_3O_4 thin film annealed at 350˚C for 20 minutes.

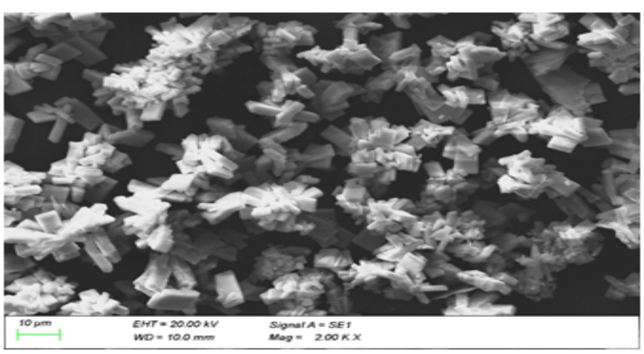

Fig. 3: SEM image of Co_3O_4 thin film annealed at 650˚C for 20 minutes.

It is also seen from Fig. 3 that the thin film of cobalt oxide on glass substrate annealed at high temperatures provides greater surface area due to its vertical growth. The enhanced surface area of the films can be used as electrodes of capacitors which is the prime requirement for supercapacitor application [24]. There are many small grains with cracks and uncovered areas on the substrates at low temperature annealing. These smaller grains coalescence to form bigger grains and film surface becomes smooth during high temperature annealing.

3.3. Optical Band Gap Determination

To determine the band gap of the cobalt oxide thin film, optical absorption in the UV-VIS is recorded. The dramatic change of absorption in the visible region indicates the direct absorption band gap transition in Co_3O_4 films. Optical band gap energy is calculated from absorption spectrum data using the following Tauc's formula $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$; where, α is the absorption coefficient, hν is the photon energy of the light, A is a constant, E_g is the band gap energy of the materials under investigation and n is also a constant whose value is 1/2 for direct allowed energy band transition [25]. Using this relation, graph is plotted between the square of (αhν) and hν as shown in Fig. 4.

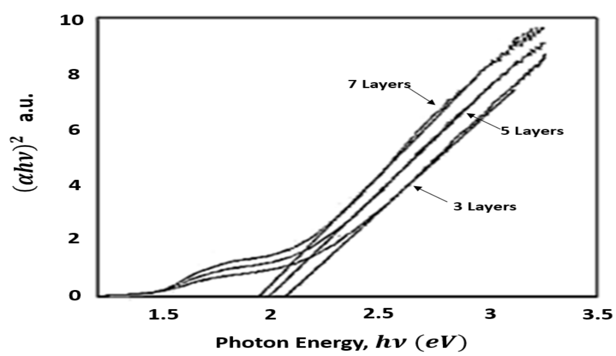

Fig. 4: Plots of $(\alpha h\nu)^2$ against hν of Co_3O_4 thin films with different layers annealed at 350˚C.

The extrapolation of the straight line drawn on the above curve intersect to energy axis gives the value of the band gap energy. The linear part of the square of (αhν) and hν graph indicates that the energy band gap of the cobalt oxide thin films is direct in nature. The presence of direct band gap in cobalt oxide may be due to the degeneracy in the valence band [25–27]. It is observed from the study that the value of optical band gap varies slightly with film thickness and are in the range 1.9–2.1 eV. It is noticeable from the figure that the band gap E_g increases from 1.9 eV to 2.1 eV with the increase of film thickness.

Density of localize states and grain size depend on the variation of temperature and film thickness. Film thickness and heat treatments can change the localized states in the films and hence the energy band gap because localized states. The film thickness also affect the grain size and hence influence the energy band gap. The grain boundary scattering has decreased with the increase of film thickness. The scattering of carriers at the grain boundary of the film decreases as the film thickness increases [28]. The increase of band gap energy with the increase of film thickness can be explained with the help of the increase of particle size in the crystallites along with reduction of porosity in the film. Therefore, the variation of optical energy band gap in the cobalt oxide film may be due to the variation of localized states and grain size.

3.4. Electrical Property Analysis

The electrical properties of Co_3O_4 film are carried out by four probe methods. Fig. 5 shows the I–V Characteristics of Co_3O_4 thin films with various measurement temperatures. The samples were annealed at 350˚C in open air. It is seen from the I-V graphs that the current increases with the increase of voltage. It is found that the electrical resistivity of the films is 0.018 Ω–cm at room temperature. At a constant potential difference of 6V across the sample, the current in the sample increases from 22 μA to 45 μA when the temperature increases from 90˚C to 160 ˚C. The I-V characteristics at various temperatures indicate the semiconducting nature of the film [5].

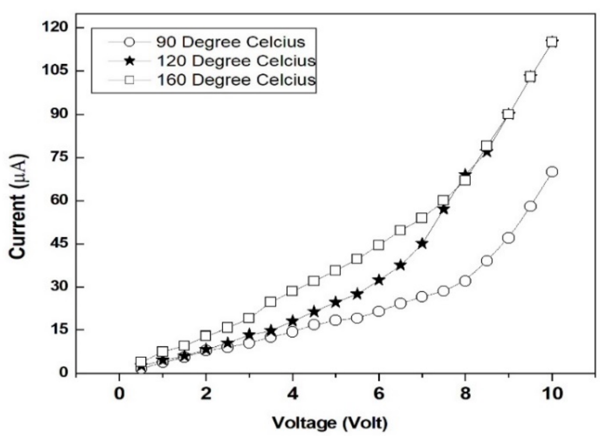

Fig. 5: I–V Characteristics of Co_3O_4 thin film with different measurement temperatures annealed at 350˚C.

4. Conclusions

Cobalt oxide thin films have been prepared by using sol-gel method on glass substrate. All as–deposited films are heated at 60˚C for two hours before final annealing. Strong peaks in the XRD result revealed that the structure of Co_3O_4 thin film is polycrystalline in nature with cubic structure. The strongest peaks that appear from (311) plane indicate the preferential direction of crystal growth in the grain of Co_3O_4 thin film. It is found from our measurement that the average value of the crystallite size is about 75 nm. It reveals from the SEM images that nanocrystalline grains with flake types of structures are present in the thin films annealed at higher temperatures. It is also seen from the morphological study that the surface grows vertically and becomes smooth at higher annealing temperature. The energy band gap of cobalt oxide thin films is found to be 1.9–2.1 eV. It depends on the film thickness. It is found that the electrical resistivity of the film at room temperature is 0.018 Ω–cm. Electrical measurements show that the annealed Co_3O_4 films are semiconductors in nature. The increased surface area due the vertical growth and porous surfaces of Co_3O_4 films may be a very good candidate for supercapacitor application.

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