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RESEARCH ARTICLE

INFLUENCE OF ANNEALING TEMPERATURE ON OPTICAL PROPERTIES OF CaO THIN FILMS

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ABSTRACT

Nanocrystalline Calcium oxide (CaO) thin films were synthesized on glass substrate by using chemical bath deposition (CBD) method. The variation in structure, morphology, and optical properties of CaO thin films annealed at various temperatures were analyzed in detail. The film showed a high transmittance (60%) and a wide band gap ranges from 3.62 to 3.39 eV.

INTRODUCTION

Nanostructures coating with controlled surface area, porosity, crystalline orientation, grain size and surface morphologies are desirable for many applications, including microelectronic device, energy conversion and storage, LED, imaging techniques and catalysis [1]. A variety of techniques has been employed to grow Calcium oxide nanostructures directly on the substrates. Among them, chemical bath deposition was formed to be a cost-effective and easily scalable method and can be widely applied for the direct synthesis of CaO nanostructures rather than the conventional Physical Vapor Deposition techniques. The choice of this technique centers largely on the fact that it possess a number of advantages over conventional thin film deposition methods, such as low cost, low temperature and easy coating of large surfaces. The technology is based on the controlled release of the metal ions. In the case of oxide films, the deposition follows a two-step process: deposition of the hydrous film and its pyrolytic decomposition into the anhydrous film [2]. Also according to existing literatures there are two methods have been reported on the preparation of calcium oxide thin film. One of them is thermal decomposition [3-5] and the other is sol-gel method [6]. This paper reports on the preparation and optical properties of calcium oxide thin film deposited using chemical bath deposition technique [7-9].

EXPERIMENTAL ANALYSIS

In this study the CaO thin films were prepared using the chemical bath deposition technique. The chemical bath deposition system was made up of 50ml of 0.1M calcium nitrate, 30 ml of 0.1M hydrazine hydrate and 30ml of 0.1M triethanolamine (TEA) which acts as a complexing agent. Solutions for the deposition bath were made in 100ml beakers and 76mm x 26mm x 1mm commercial quality glass slides were used as the substrate. The glass slides were soaked in a solution of nitric acid and then washed thoroughly with detergent and rinsed with distilled water.

After transferring the solution into a beaker, the substrates were suspended vertically in the solution. After 5 hours the films were removed and washed after deposition and allowed to dry in air. Uniform films were obtained in this process. Even though the thin film samples were deposited at room temperature, some of the films were subjected to post deposition annealing at the temperatures of 200˚C, 300˚C, and 400˚C. The optical absorbance and transmittance of the samples were investigated in the UV-VIS-NIR region.

RESULT AND DISCUSSION

Surface Morphological Analysis

The SEM images of CaO thin films prepared at various temperatures are shown in figure 1(a-d). These micrographs showed that the cube like structure for as deposited film and there was a change in size after annealing the films. Also when we increase the annealing temperature at 300˚C the grain size was increased and we get the closely packed structures.

Structural Analysis

Figure 2 (a-d) shows the X-Ray diffraction patterns of the as deposited and annealed calcium oxide thin films on glass substrates. The d-values of the lines obtained from the XRD pattern have been compared with the corresponding values for calcium oxide in the JCPDS (28-0775) data file. The derived d-values are in good agreement with the standard value, which confirms that the film constitute CaO. In order to prove the nanometer size of grain, the Scherrer method has been used. The average crystalline size of 100 nm was determine by measuring the full width at half maximum of peaks and using the Scherrer formula [10].

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$$\alpha = \frac{K\lambda}{D\cos\theta}$$

Where 'λ' is the wavelength used (1.54A), β is the full width at half maximum peak, D is the diameter of the grain and K is a constant. Optical absorption spectra and SEM micrograph have shown that the films were formed from nanometer grains.

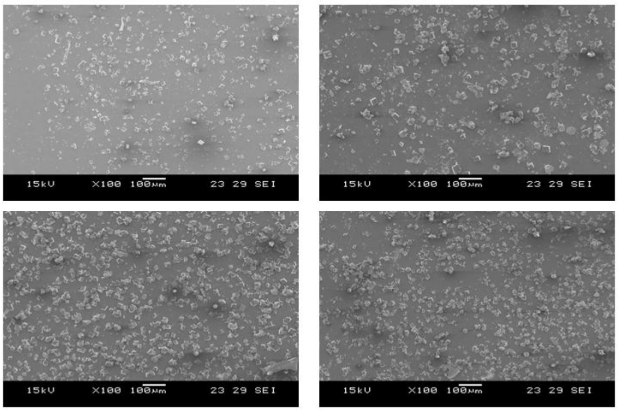

Figure: 1.SEM Micrograph for (a) room temperature (b) at 200˚C (c) at 300˚C (d) at 400˚C.

Optical Properties

CaO thin films were deposited on glass substrate using chemical bath deposition. From figure 3 & 4 the films deposited at the various annealing temperatures displayed high transparency in the visible to near-infrared regions with little or no difference in optical transparency. The average transmittance in the visible region is more than 60%. In general, the films show very high degree of transmittance and very low degree of absorption in the entire spectral regions.

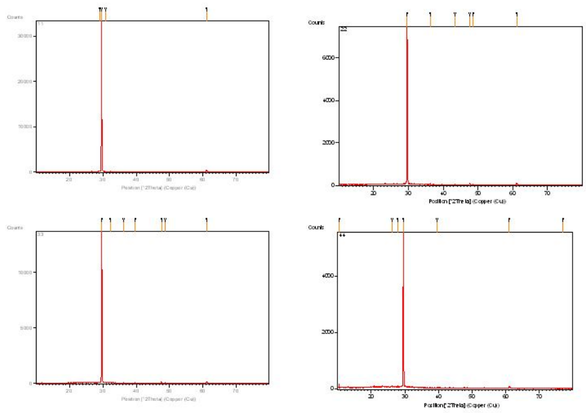

Figure: 2.XRD Spectra of (a) room temperature (b) at 200˚C (c) at 300˚C (d) at 400˚C.

The optical band gap of the thin film is determined from the transmittance vs. wavelength plot. The relation between the absorption coefficients (**α**) is given by

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d}$$

Where **T** is transmittance and **d** is film thickness.

The relation between the absorption coefficient and the incident photon energy **(hν)** is given by the following equation

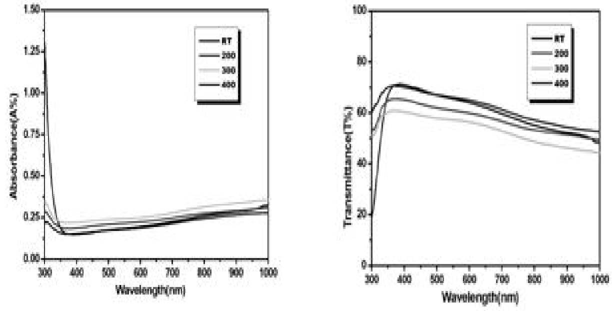

Figure: 3 & 4. Optical absorption and transmittance spectra for various annealing temperature.

Where **'Eg'** is the direct transition band gap and **n = ½** for direct allowed transition

Figure 5 (a) shows a plot of **(αhν) ²** against the photon energy **hν.** From the results shown in Figure 5(b**)**, it is observed that the direct optical band gap for CaO films decreases from 3.62 to 3.39 eV as the annealing temperature increases.

The band gap obtain for various annealing temperature are shown in the table below:

Sample	Annealing Temp	Bandgap (ev)	Particle size(nm)
CaO-1	Room Temp	3.62	60
CaO -2	200˚C	3.48	111
CaO -3	300˚C	3.43	217
CaO -4	400˚C	3.39	402

The table shows a decreasing band gap with increasing temperature. Even the decreased values of **Eg** still remain wide. The reduced band gap upon the thermal treatment is related to the effects of increased particle size.

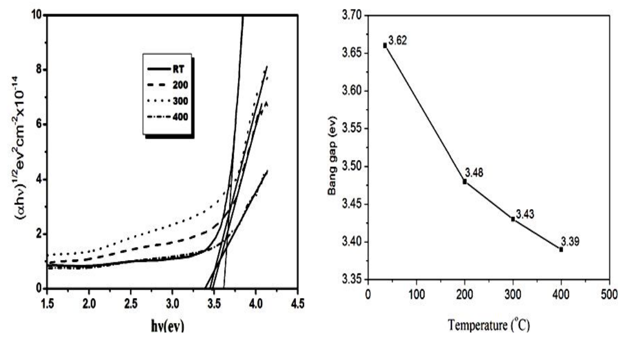

Figure: 5. (a) Plots of (αhν) ² Vs hν for CaO films grown at different temperature, (b) The variation of bandgap with annealing temperature

Photoluminescence Properties

The effect of the thermal annealing on the light emission properties of CaO films was investigated. Fig. 6 shows the PL spectra of the CaO films. From this figure, a ultra-violet near-band edge emission peak near 375 nm and defect related deep-level emission around 480-500 nm from the CaO films were observed. The UV emission peak originated from excitonic recombination as shown by other researchers, and the UV peak intensity varies with annealing temperatures. Defect-related green emission is believed to come from oxygen vacancies.

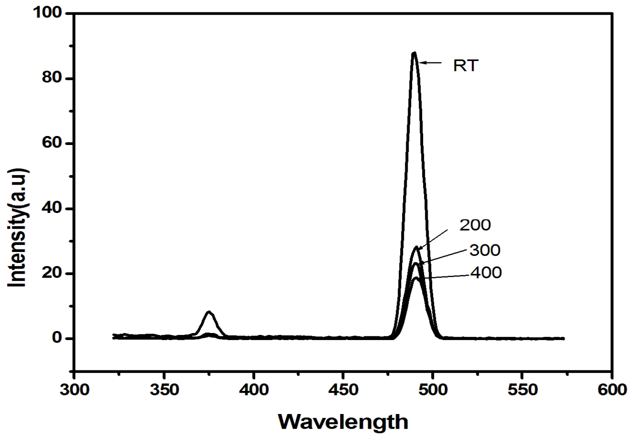

Figure: 6 PL spectra of CaO thin films.

CONCLUSION

CaO thin films have been deposited by chemical bath deposition technique using calcium nitrate, TEA, hydrazine hydrates solutions. Post deposition annealing of the films at temperatures 200^{o} C, 300 ^{o} C and 400 ^{o} C sharpened the properties of the films. CaO film is a transparent oxide film. The transmittance increases from UV-NIR regions up to over 60 %. The absorbance is generally low and increases within the same region. Band gap varies from 3.62 to 3.39 ev, were obtained for the oxide film under different annealing temperatures. The values are in agreement with theoretical values. The outstanding properties of the oxide films show them as good materials for solar cells, gas sensors, as well as transparent electrodes for panel display etc.,

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