



RESEARCH ARTICLE

INFLUENCE OF THE PARTICLE SIZE ON THE OPTICAL PROPERTIES OF CaO THIN FILM

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ABSTRACT

Calcium Oxide (CaO) thin layers with the same deposition conditions were deposited on glass substrates at room temperature. Different deposition time period namely, 4hr and 24hr were used to produce Calcium Oxide film. The CaO thin films were studied using SEM and XRD methods. Optical properties were studied by spectrophotometer method. The size effect plays an important role on structural and optical properties of layers.

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INTRODUCTION

Recently, inorganic antimicrobial agents are being increasingly for control of microorganism in various areas, especially in dentistry. Particle size of metal oxides had an impact on their anti-microorganism activity. There is growing interest in nanoscale particles ever since materials exhibit unique properties which offer considerably from those of macroscopic materials. Inorganic nano metal oxides including MgO, ZnO and CaO have been shown anti-microorganism activity. It has been shown that properties of inorganic nano-materials depend heavily on their morphologies. Therefore, the design and controlled synthesis of nanostructures with different morphological configurations and size distribution, on a large scale, are very imperative from the viewpoint of both basic research and technological applications [1–4]. With a potential for has wide range of applications CaO metal-oxide is of continuous interest in the field of materials research. Pure CaO shows cubic lattice structure [5] with anisotropic catalytic properties. It is also often investigated as a component in catalytic powder materials and cements [6]. In addition, CaO is known as dopant that is able to stabilize metal-oxides like cubic zirconia [7] and hafnia [8]. Its also used to modify the refractive index of silicate glasses [9]. Due to its wide band gap [10], high dielectric constant [11] and the ability to form solid solutions and ternary crystalline phases, CaO and their ternary alloys can be considered as interesting dielectric gate materials, exhibiting high mechanical and radiation resistance [12]. However, only a very little has been reported on the preparation of nano-CaO. Primarily, two methods have been reported on the preparation of nano-CaO according to the existing literatures. One is thermal decomposition [13-15] and the other is sol-gel [16]. In the present paper we report the influence of particle size variation on the optical properties of CaO nanoparticles. The CaO nanoparticles were prepared by chemical method. The results of X-ray diffraction (XRD), absorption spectra and photoluminescence emission spectra are presented and discussed.

Experimental details

CaO thin films have been deposited on commercial glass substrates using CBD technique. The deposition solution was prepared by mixing solutions of CaCl_2 (0.5 mol) and hydrazine hydrate (0.5mol) and adjusting the pH to the value of 9 with KOH. In order to achieve a good adhesion of the coating material onto the substrates surface, special attention was paid to the preparation of substrates. A standard procedure was adopted for the cleaning of the substrates prior to the CBD process in order to achieve reproducible results. The mixture was kept at room temperature, after formation of film; the slide was taken out, washed with water and air dried. The films thickness can be controlled from 50nm to 150nm by the duration of deposition.

RESULT AND DISCUSSION

The as prepared film are adherent well to the substrates. Figure 1 shows the XRD patterns of CaO film deposited at room temperature. The film shows a good crystalline structure. Figure 1 shows a single diffraction peak at 29.26° indicating a preferred orientation along (1 1 1) plane of reflection corresponding to the cubic phase. This preferred orientation of CaO is due to the controlled nucleation process associated with the low deposition rate. This (1 1 1) peak at 29.26° was only obvious one for the films having particle size in microns and nano, while size reduction further enhanced its intensity. Scanning electron micrograph was obtained from film of CaO is depicted in figure 2. The SEM image shows evidence for decrease in the grain size with decreasing dip time. Figure 3 shows the absorbance and transmittance spectra of CaO film. As can be seen from Fig. 3, these films are highly transparent in the visible region and present a steep absorption edge at a wavelength of about 330 nm. It can be seen that the film is highly transparent in the visible region of the electromagnetic spectrum with an average transmittance greater than 85% for the wavelength values over 400nm. These high transmittance and low reflectance properties make the film good material for antireflection coatings and for solar thermal applications.

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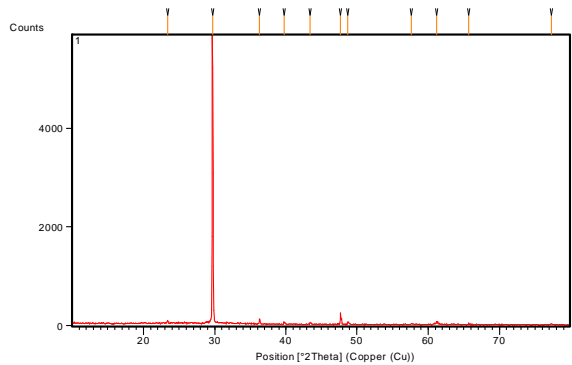
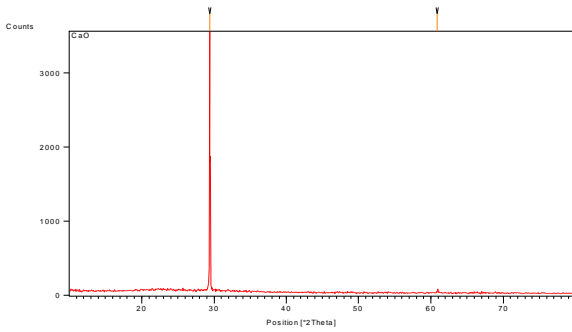
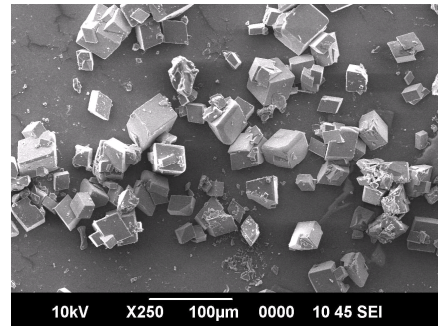


Figure 1: XRD images for CaO films at different deposition time (a) 4 hrs (b) 24hrs



(b)

Figure 2 : (a) and (b) close together

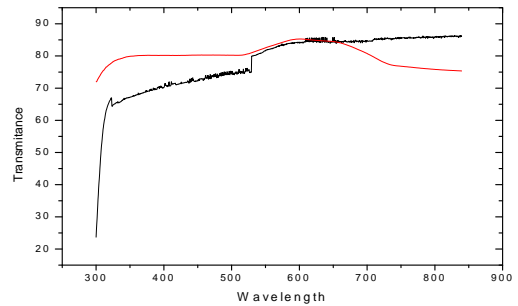
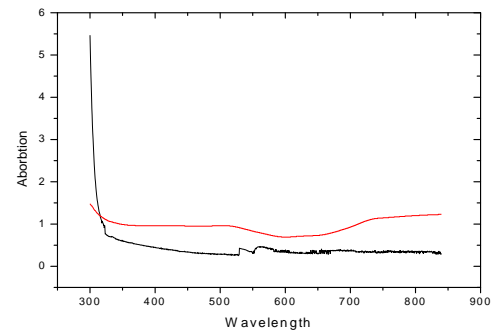
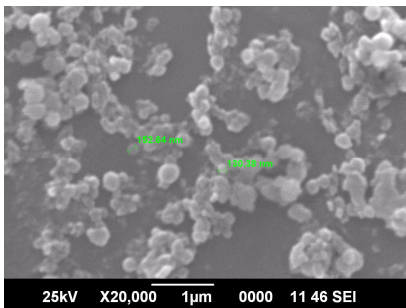


Figure 3 Optical absorption and transmittance spectrum of CaO films at different deposition time 4 hrs and 24 hrs

The optical properties are strongly dependent on the particle size. It can be seen from the spectra that there is practically uniform absorption and transmittance in the visible range (790-390 nm) and (390-700nm). Absorption increases suddenly in the UV region. Transmittance increases in the green region for the film having particle size in micron. In addition, the transmission between 600 to 800nm decreases with the smaller the size of CaO particles. A comparison between the transparencies of the films cannot be directly made because of the different film thicknesses.



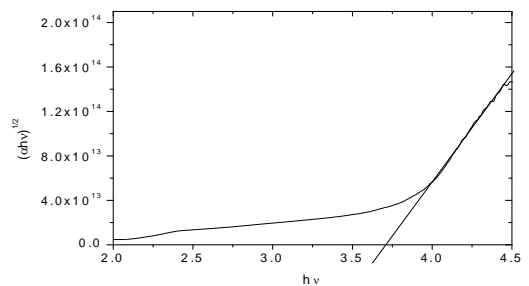
(a)

The absorption data were analyzed using the well known relation for near edge optical absorption of semiconductors:

$$\alpha h\nu = \frac{A(h\nu - E_g)^n}{h\nu}$$

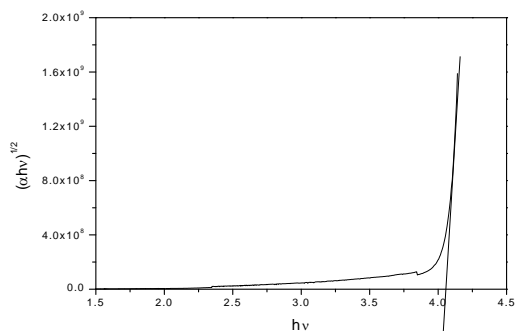
where 'A' is a constant, 'E_g' is optical band gap of the material and the exponent 'n' depends upon the type of transition. The values of 'n' for direct allowed, indirect allowed and direct forbidden transitions are n = 1/2, 2, and 3/2, respectively. To understand the onset of high photon energy corresponding to the direct band gap we plotted (αhν)² plotted as a function of photon energy hν as shown in Fig. 4. Linearity of the plots indicates that the material is of direct band gap nature. Extrapolation of linear portion of the graph to the energy axis at α = 0 gives the band gap energy E_g, which is 3.6eV.

The change in shape from spherical to trigonal morphology, as evident from the SEM micrographs, leads to a non-monotonous change in the visible emission energy of their PL spectra (excitation at 325 nm). In figure 5, we show the emission spectra over the entire visible range.



(a)

The emission in the range 340-360 nm is the near band edge emission. It can be seen that the blue-green emissions in the range 400 nm - 450 nm show distinct emission energies as the particle size as well as the shape changes. Emission bands red shifted from the absorption edge are observed in both films. These red shifted emissions are usually associated with trapped states such as vacancies, interstitials, impurities, and surface defects.



(b)

Figure 4 $(\alpha hv)^2$ Vs $h\nu$ for CaO films at different deposition time (a) 4 hrs (b) 24 hrs

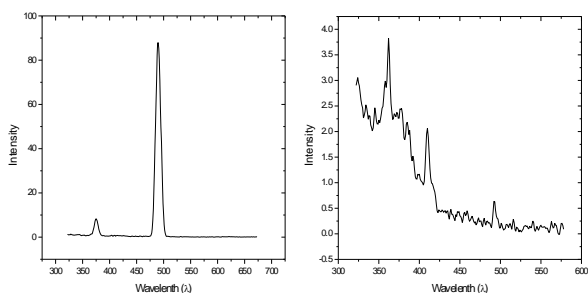


Figure 5 PL Spectra for CaO Films at deposition time (a) 4 hrs (b) 24 hours

CONCLUSION

Because of importance of some of alkaline-earth metal compounds in industry and medicine, in this work we tried synthesis nanostructures CaO. To summarize, we find that CaO nanoparticles undergo a shape change. The change in shape is associated with a collapse of the microstrain. It also leads to a sharp change in the blue-green emission band from CaO nanostructures.

PL spectrum excited by 300 nm shows a Stoke shifted peak in UV region. For smaller average size, there is larger distribution of nanocrystalline sizes, causing bluish green PL peak. The characteristic change of the band gap with decrease in size of the nanostructures cannot be observed because of the different film thickness.

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