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Synthesis of barium oxide nanorod by chemical bath deposition

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Abstract

We report on the control of nanocrystal sizes in barium oxide nanorods prepared by chemical bath deposition technique. Barium chloride and potassium hydroxide are used as source materials to obtain barium oxide films. Different chemical baths are used to study changes in the structures of the BaO films The effect of hydrazine hydrate on growth of these films has been studied. The results reveal that the additive played a very important role on crystalline size and shape.

Key Words: Thin films, nanostructures, chemical synthesis, optical properties

1. Introduction

Nanoelectronic devices assembled from structures such as nanorods, nanotubes and nanowires have tremendous potential for a wide range of applications. They may serve as detectors in chemical and biological sensing applications or as interconnects in high density molecular electronic circuits. The unique electronic and optical characteristics that arise in low dimensional semiconductor nanostructures due to quantum confinement are also of interest for devices such as quantum transistors and nanoscale light emitters.

The ability to control the particle size [1–4], shape, surface, structure [5] and morphology of nanoparticles [6, 7] is of crucial importance both from a fundamental research and their implementation in technological devices. Relatively recently, researchers have begun to understand how to control the nanocrystal shape, producing low aspect ratio nanorods, very high aspect ratio nanowires and complex branched structures.

Thin film formation of these structures can be carried out by various methods which include sol gel [8], chemical vapour deposition [9, 10], pulsed-laser deposition [11], vacuum arc deposition [12] and chemical bath deposition (CBD) technique [13–15].

Recently, there has been considerable interest in developing new metal oxide thin films using various techniques. Among them, the chemical bath technique appears to be a relatively simple, inexpensive method to prepare a homogenous film with controlled composition. However, depending on the deposition conditions

like pH of the solution, temperature, composition, stirring, and time of deposition, the quality as well as the stoichiometry of the film differ and hence their structural and optical properties

This review focuses on the evolution of the synthesis BaO [16–19] nanorods that may serve as building blocks for future nanoscale devices.

2. Experiment

BaO thin films were deposited on glass substrates using chemical bath deposition (CBD) method at room temperature. The substrates used for the deposition are commercial glass slides of 76 mm × 25 mm. The glass substrates were cleaned with nitric acid, detergent solution and distilled water. Prior to deposition, the substrate was etched in concentrated HF for 5 min, rinsed with double distilled water and dried.

To investigate the influence of additive hydrazine hydrate on the microstructure of the film we prepared two different aqueous alkaline solutions without and with hydrazine hydrate. In the first solution, the solution contains 0.1 M barium chloride ($BaCl_2$) and 0.1 M KOH. The second solution differs from the first solution by the addition of hydrazine hydrate as the solution buffer. The glass slides were kept vertically in the beaker. The growth time for each bath was 24 hours. After the deposition, the BaO films were washed with distilled water to remove the loosely adhered BaO particles on the film and finally dried in air.

3. Result and discussion

3.1. Surface morphological analysis

The surface morphology of films synthesized with and without the additive hydrazine hydrate was carried out by scanning electron microscope (SEM), shown in Figure 1. From the image, it can be seen that the BaO nanorods were embedded into the glass substrate. Fine nanorods were observed for the first group of solution (see Figure 1(a)). For the buffer solution with hydrazine hydrate (see Figure 1(b)), we observed that the particle was uniformly deposited over the substrate and the nanorod thickness was reduced. It was also found that the shape and size of the nonorods were very uniform. The results infer that the particle size and crystallinity of the film were effectively tailored by hydrazine hydrate.

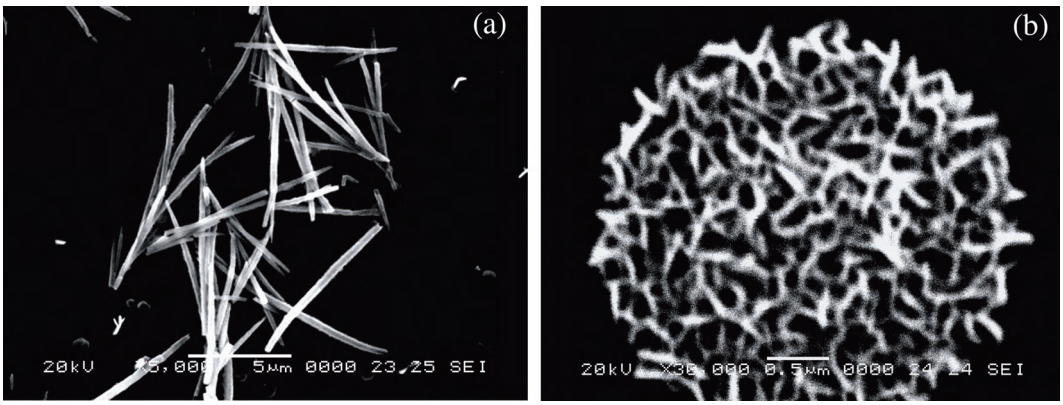

Figure 1. SEM micrographs showing the presence of BaO nanorods as formed under (a) 0.1 M concentration $BaCl_2$ and KOH, and (b) as formed under the presence of hydrazine hydrate.

3.2. Composition analysis

Quantitative analysis for energy dispersive X-ray analysis (EDAX) was performed for Barium (Ba) and Oxygen (O) on various samples; the EDAX data is plotted in Figures 2(a) and 2(b). The elemental ratio of Ba and O are found to be approximately the same from peak area analysis, giving rise to the fabrication of correct stoichiometric films. Compositional analysis clearly confirmed that Ba and O were present in the film.

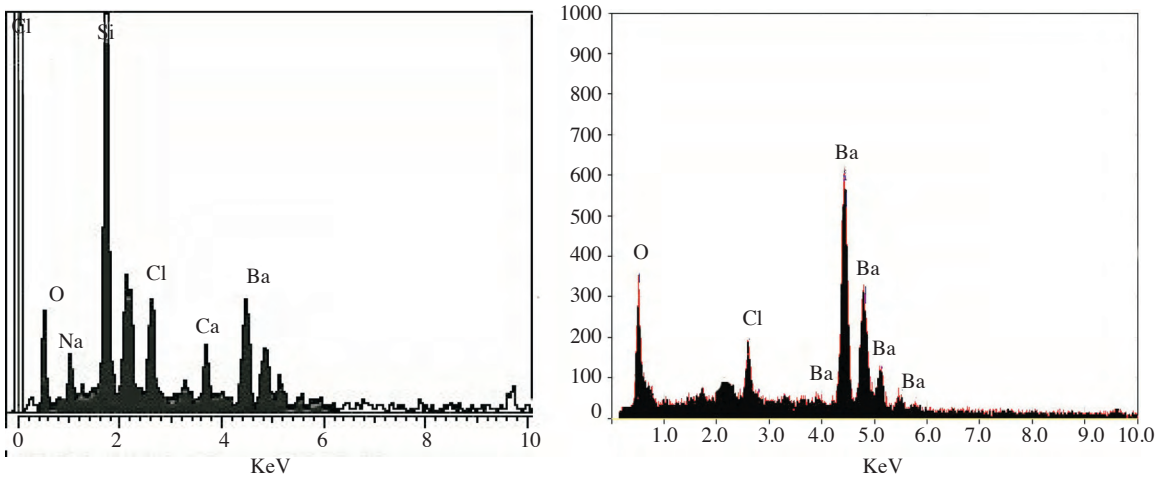

Figure 2. EDAX spectrum for (a) 0.1 M concentration $BaCl_2$ and KOH, and (b) in the presence of hydrazine hydrate.

3.3. Structural analysis

X-ray diffractograms of the BaO thin films deposited from two different solutions are displayed in figure 3(a-b). Figure 3(a) shows the XRD patterns of the as-prepared film on glass substrate for 0.1M $BaCl_2$ and 0.1M

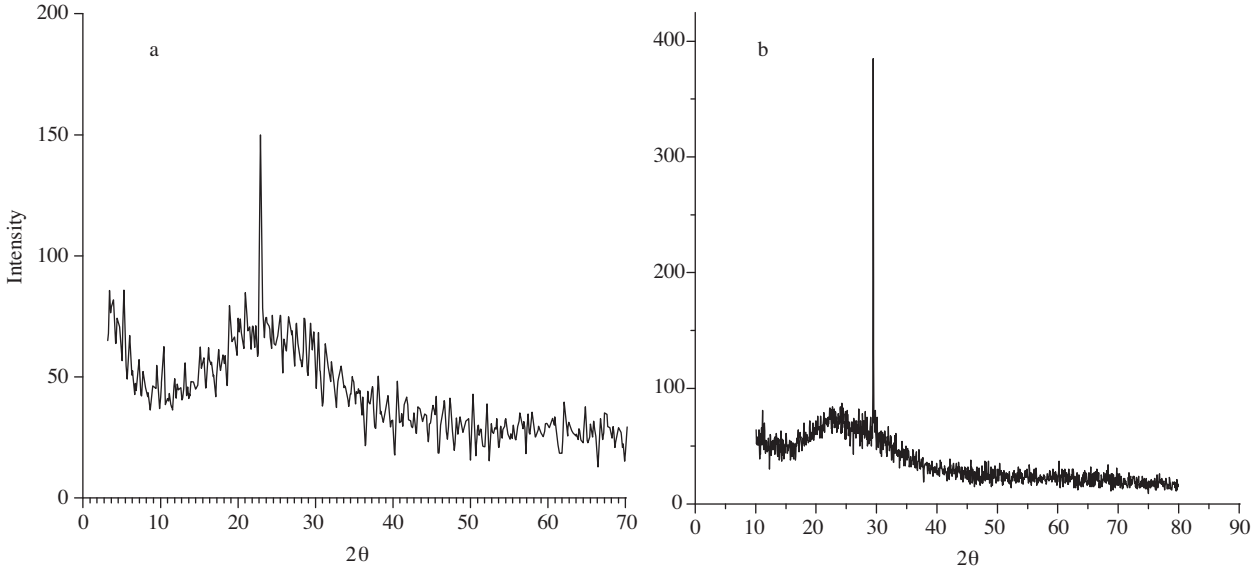

Figure 3. XRD spectra of (a) 0.1 M concentration $BaCl_2$ and KOH, and (b) in the presence of hydrazine hydrate.

KOH. The observed diffraction peaks were compared against standard JCPDS diffraction patterns database. The observed values of d in the film were in good agreement with those reported in the JCPDS data file for BaO (47-1488).

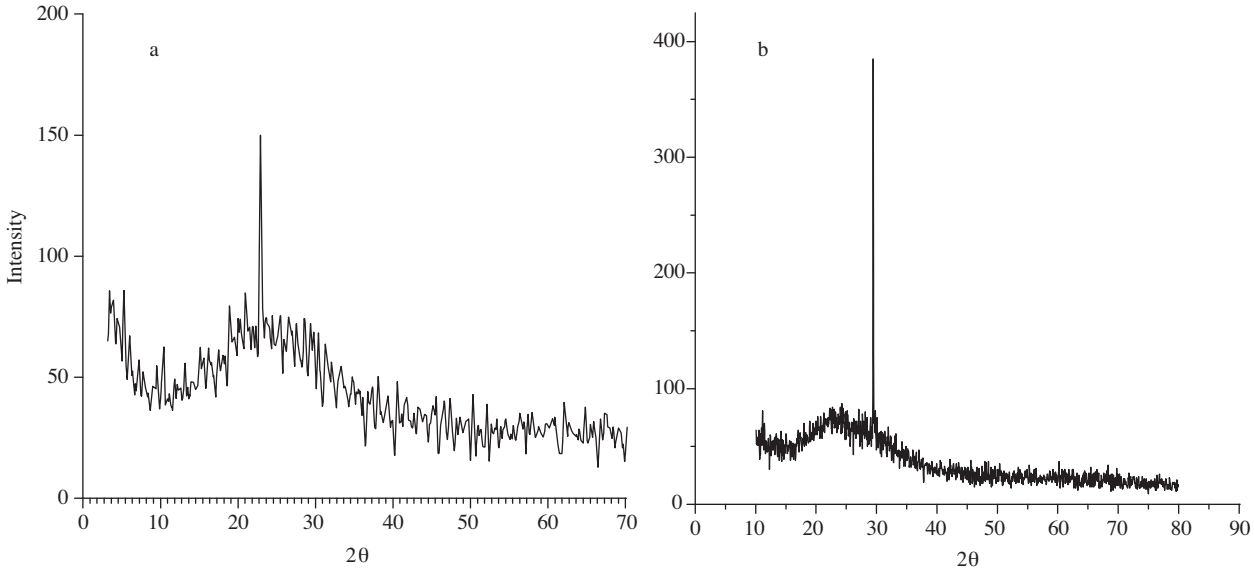

Figure 3. XRD spectra of (a) 0.1 M concentration $BaCl_2$ and KOH, and (b) in the presence of hydrazine hydrate.

Figure 3(b) shows X-ray diffraction spectrum for the BaO film in the presence of hydrazine hydrate. It consists of well-defined diffraction peak of barium oxide, indicating that a thin crystalline single phase BaO thin film is deposited onto the glass substrate. Calculated values of d are in agreement with JCPDS data (47-1488). The spectrum indicates that the BaO film is crystalline in nature. The grain size for the sample with Hydrazine hydrate was calculated by means of Scherrer's equation

$$d = \frac{0.94\lambda}{\beta cos\theta},$$

where λ is the wavelength used (1.54 Å), β is the angular line width at half maximum intensity in radians and θ is Bragg's angle. Using Scherrer's formula, grain size was found to be of the order of 49 nm.

3.4. Optical properties

Figure 4 shows a comparison in the optical transmittance spectra of the BaO films, without and with additive. As can be seen from Figure 4, these films are highly transparent in the visible region and present a steep absorption edge at a wavelength of about 330 nm. The figure shows that the addition hydrazine hydrate influences the optical properties of the film. The average optical transmittance in the visible region (500 to 1000 nm) is 80% for the film without the additive, which increases to 90% after the addition of hydrazine hydrate. Also, the effect of additive led to a shift of the fundamental optical absorption edge towards the UV region. As it is clear from figure the films have a steep optical absorption edge feature, indicating good homogeneity in the shape and size of the grains and low defect density near the band edge.

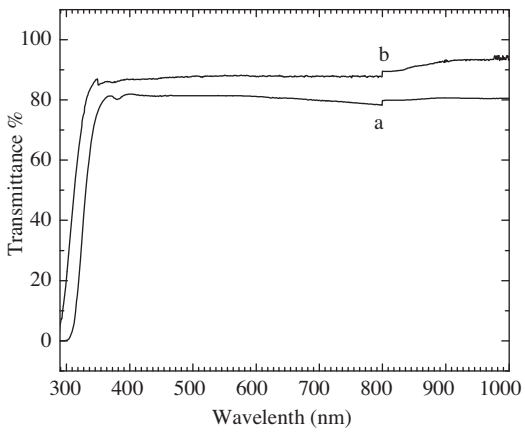

Figure 4. Optical Transmittance spectra of (a) 0.1M concentration of $BaCl_2$ and KOH (b) in the presence of hydrazine hydrate.

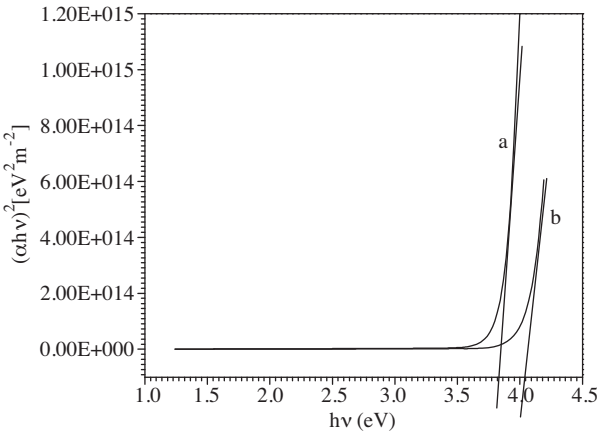

Figure 5. Plots of $(\alpha h\nu)^2$ as a function of $h\nu$ for samples (a) without hydrazine hydrate (b) with hydrazine hydrate.

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

$$\alpha h\upsilon = \frac{A(h\upsilon - Eg)^n}{h\upsilon}.$$

Here, A is a constant, E_g is the 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 $(\alpha h\nu)^2$ as a function of photon energy $h\,\nu$ in Figure 5. The variation of $(\alpha h\nu)^2$ versus hν in Figure 5 is linear at the absorption edge;a the linearity indicates that the material is of direct band gap nature. The band gap energy is obtained by extrapolating the linear portion of the plot to the crossing with $h\nu$ axis. The estimated direct band-gap value for the film without hydrazine hydrate is 3.8 eV which increases to 4.1 eV for the film with hydrazine hydrate.

4. Conclusion

We presented a simple and economic technique that offers a possibility for synthesis of BaO nanorods at a fairly low temperature. BaO nanorods are prepared by chemical bath deposition from an aqueous solution containing $BaCl_2$, KOH. In order to obtain good quality and cheaper metal oxide thin films, influence of composition have been studied. It was observed that for all BaO film studied, their quality improves with addition of hydrazine hydrate. Addition of hydrazine hydrates with solution-buffer decrease the grain size and consequently the quality of the films.

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