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Synthesis and characterization of vertically aligned cadmium oxide nanowire array

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Abstract High density and ordered cadmium oxide (CdO) nanowire array has been synthesized using anodic aluminium oxide template by electrodeposition method. The optical, morphological and structural properties of nanowire array and planar thin layer have been studied with the help of UV–Vis spectrophotometer, photoluminescence spectrometer, scanning electron microscopy and X-ray diffraction. The results obtained from nanowire array are compared with the planar thin layer of CdO. Preferentially oriented along (200) plane with face centered cubic crystalline nanowires are synthesized. The uniform and vertically standing nanowire array of diameter ~50 nm and length ~2.5 μm was prepared. UV–Vis spectroscopy analysis confirms the direct gap of the CdO nanowires were found to be ~3.20 eV which is higher than the bulk CdO for direct band gaps (2.48 eV) due to quantum confinement effect. The CdO nanowire array has high transmittance over 80 % in visible region as compared to 55 % in case of CdO film. The direct band transition and exiton emission to nanowire array was observed at 440 and 510 nm, respectively.

1 Introduction

Transparent conducting metal oxides are fundamental to the development of smart and functional materials, which are candidates for optics, optoelectronics, and chemical, biochemical and environmental sensors as well as transducers. The oxides have two unique structural features: switchable and/or mixed cation valences, and adjustable oxygen deficiency, which are the bases for creating many novel materials with unique electronic, optical, and chemical properties. The oxides are usually made into nanoparticles or thin films in an effort to enhance their surface sensitivity, and they have recently been successfully synthesized into nanowire-like structures. Utilizing the high surface area of nanowire-like structures, it may be possible to fabricate nanoscale devices with superior performance and sensitivity.

Cadmium oxide (CdO) is n-type degenerate direct band gap II-VI semiconductor with band gap 2.28 eV [1, 2]. Large shift of fundamental optical absorption edge from 2.25 to 2.49 eV is observed with increasing the carrier concentration. CdO is a promising functional material for various optoelectronic devices due to its high electrical conductivity, high carrier concentration and high optical transmittance in the visible region of the solar spectrum [3].

They can be used for display screens, optoelectronic, photonic, and photovoltaic devices due to their unique dual transparent and conductive properties [4–6]. For nanophotonics applications, it is desirable to fabricate structures with controlled size, periodicity, crystallinity, geometry, and alignment. Consequently, it is important to develop nanofabrication techniques to achieve the above specified structures. CdO nanowire arrays can be applied as a transparent electrode in the solar energy devices due to their high surface area and good vertically aligned electrical pathways, which are expected to increase the efficiency of these photoelectric devices [7–9].

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2 Experimental section

2.1 Preparation of nanoporous alumina membrane

Nanoporous alumina membranes were fabricated by anodizing aluminium foils potentiostatically in sulphuric acid at 0 °C for 10 min using lead plate as cathode [10]. Anodization produced porous membrane of hexagonal shape having pores almost perpendicular to the membrane surface.

2.2 Preparation of CdO nanowire and planar thin layers

Two electrode electrochemical system was employed to prepare CdO nanowires and planar thin layer of CdO. The aqueous solution of 40 g/L $CdCl_2$ and 30 g/L H_3BO_3 was used for the synthesis of nanowires and planar thin layer of CdO. The pH of the solution was adjusted to 2–3 by using NaOH. The electrodeposition was performed using EG and G potentiostat/galvanostat (Model 362) at constant current density 1 mA/cm^2. A platinum plate was used as counter electrode. Prior to the synthesis of CdO nanowires a thin layer of Au was sputtered on one side of the alumina membrane (AM) which served as a working electrode. Commercially available Indium tin oxide (ITO) coated glass substrates (Asahi Glass Co. Japan) were used to grow the CdO layers. The deposition of nanowire and planar layer of CdO was carried out at room temperature for ~4–5 h. Both the samples were oxidized in the muffle furnace at 400 °C for 4 h and cooled down to room temperature naturally.

2.3 Characterization

The phase and crystallographic structure of the nanowire arrays and thin films were determined by X-ray diffraction (XRD) using a Philips PW3040/60 X'Pert PRO in θ–2θ coupled mode. The surface morphology was studied by Scanning Electron Microscopy (SEM) at an accelerating voltage of 20 kV, Model S-450 Hitachi High Technologies. The standing nanowire array placed on ITO coated glass substrate was fixed onto aluminum sample holder and covered with ~15–20 nm thick layer of Au by sputtered technique.

The nanowires embedded in an alumina template were transferred onto ITO coated glass substrates. The free standing nanowires were obtained by rinsing in an aqueous solution consisting Sodium hydroxide and polyvinyl pyrrolidone followed by washing several times in double distilled water and ethanol. Prior to transfer of the nanowire template onto ITO the aluminum foil from the back of template was removed with the solution of $CuCl_2$ and HCl. Supercritical drying technique was used by Liang et al. [10] to assemble the CdS nanowires vertically grown by electrodeposition technique. UV–Vis spectra were recorded in the wavelength range 300–1000 nm on a Perkin-Elmer Lambda 900 UV–Vis/NIR spectrophotometer.

Photoluminescence (PL) spectra of these samples were recorded from a computer controlled rationing luminescence spectrophotometer LS 55 (Perkin-Elmer Instruments, UK) with $\lambda_{accuracy} = \pm 1.0$ nm and $\lambda_{reproducibility} = \pm 0.5$ nm. A tunable 20 kW pulse from Xenon discharge lamp was used as the excitation source. A gated photo multiplier tube was used as a detector.

3 Results and discussion

3.1 X-ray diffraction (XRD) analysis

The structural properties of nanowire array and thin films were studied by X-ray Diffractometer Model Philips PW 3040/60 X'pert pro. The XRD patterns of nanowire array and planar thin layer of CdO are shown in Fig. 1a, b, respectively. The crystalline phase in each sample was identified by comparing with standard powder diffraction patterns (JCPDS card No. 5-0640). XRD peaks confirm the face centered cubic structure of CdO. The 2θ peaks for thin

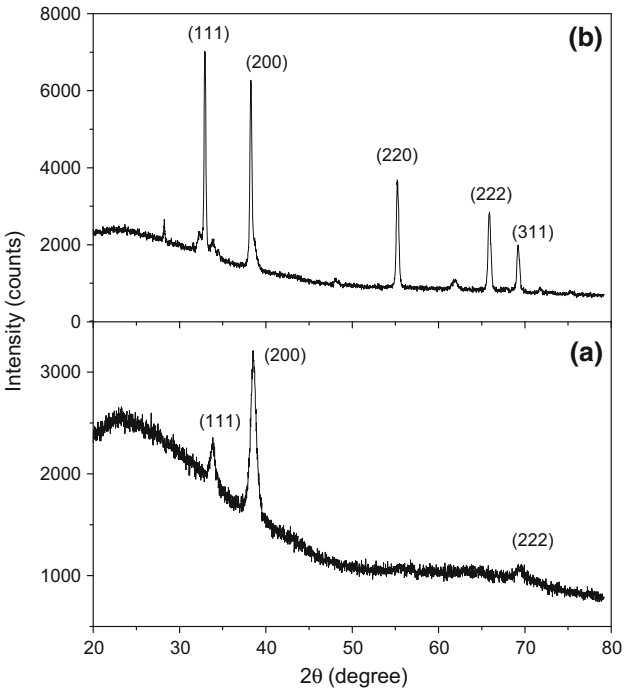

Fig. 1 X-ray diffraction spectra of **a** CdO nanowire array and **b** planar thin layer of CdO

layer were observed at 32.72°, 38.04°, 55.04°, 65.69° and 69.02° corresponds to (111), (200), (220), (311), and (222) reflections of CdO. The sharp XRD peaks indicate that the particles were of a good crystalline structure [8]. Two reflections at 32.73° and 38.09° corresponds to (111) and (200) are attributed to CdO nanowire array with preferential orientation along the (200) plane. A weak peak observed at 69.02° corresponds to (222) plane of cubic CdO. The broad hump is also observed between 20 to 30°, which is proposed due to the left over portion of alumina template. The structural analysis of nanowire array revealed the growth of nanowire is preferentially oriented long (200) plane.

3.2 Morphological studies

Figure 2 depicts the SEM image of porous alumina template a and the nanowire array grown by electrodeposition b. The porous alumina membrane with uniform hexagonal shaped pores of size ~70 nm and center to center spacing ~150 nm are prepared. It was observed that the pores were long, narrow, parallel and orientated perpendicular to the substrate. Figure 2b shows the SEM images of CdO nanowires array after removing AM template. It can be clearly observed that the CdO nanowires are highly ordered with uniform diameters ~50 nm and length ~2.5 μm. The standing nanowire array transferred onto ITO coated glass substrate is depicted in Fig. 2c. It can be clearly seen that the nanowires are standing vertically to the electrode surface in a relatively large area and the density of nanowires is almost close to the density of nanopores of alumina template. It is also apparent that the nanowires remain parallel to each other even when AM matrix was removed. This standing nanowire onto the substrate could be useful for solar cell application. The cross sectional SEM image shown in Fig. 2d was taken to determine the thickness of the planar CdO thin layer. The thickness was measured ~2.5 μm, which is very close to the length of CdO nanowires. Furthermore, the surface of the sample is relatively uneven and non-uniform.

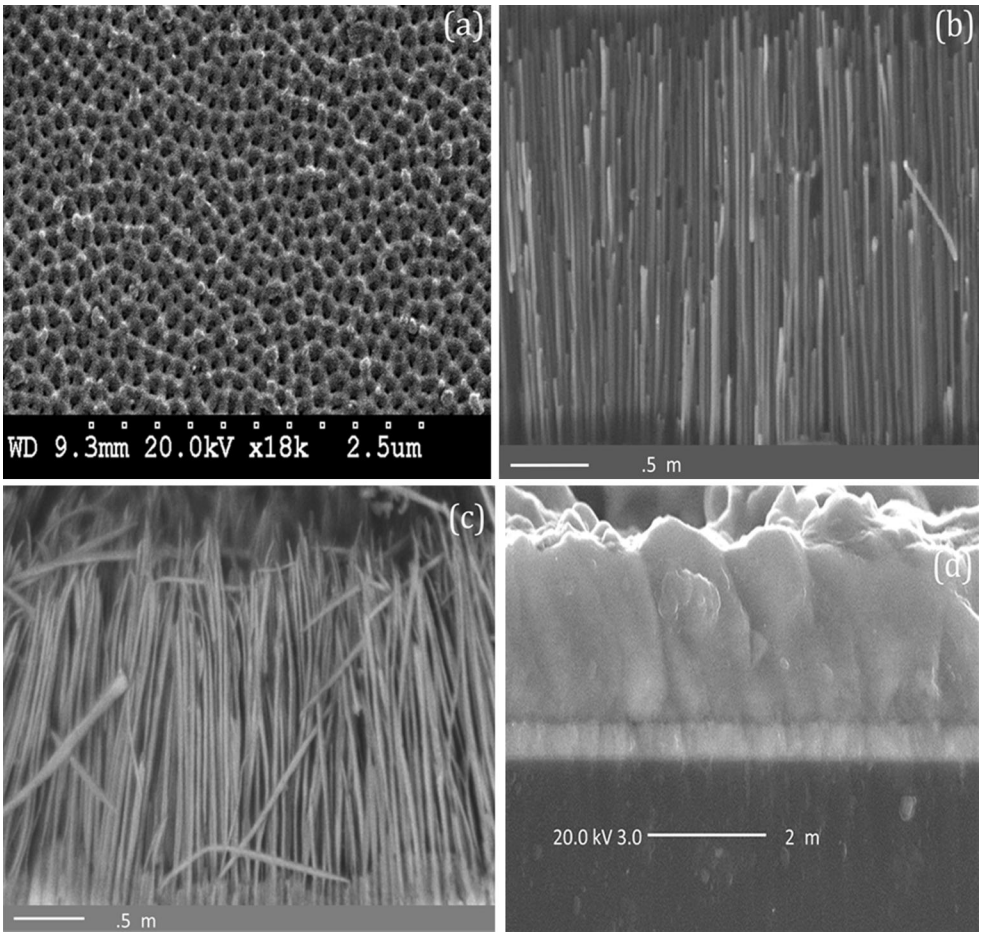

Fig. 2 SEM images of porous alumina template (**a**), CdO nanowires array (**b**), free standing nanowire array transferred onto ITO coated glass substrate (**c**) and the cross-section of planar CdO thin layer (**d**)

3.3 Optical studies

The band gap of the CdO nanowire array was estimated from the optical absorption studies. Representative optical absorption spectrum of nanowire array and planer film is shown in Fig. 3. The onset of the fundamental absorption edge is observed for the thin film at ~500 nm and found to be shifted up to 375 nm for nanowire array. The blue shift of ~0.8 eV in the fundamental absorption edge can be a signature of quantization effect [11–15]. The optical band gap that allows the transition for CdO nanowire is estimated to be ~3.2 eV. Figure 4 shows the optical transmittance of CdO nanowires and planer thin layer as the function of wavelength. Note that the length of nanowire array and thickness of planer thin layer was nearly similar ~2.5 μm (Fig. 2c, d). The optical studies revealed about 80 and 55 % average transmittance in the visible region to nanowire array and planar film, respectively. Furthermore, around 50 % enhancement in the transmittance at lower wavelength to nanowire array is also observed. The improved transmittance in nanowire array is proposed to be attributed due to two reasons: (1) the higher transmittance of aluminium oxide present in the nanowire array and (2) the blue shift in the fundamental absorption edge of CdO nanowire array. In addition, the increased transmittance in case of nanowire could also be associated to the formation of highly oriented crystal structure. The similar optical transmittance results for CdS nanowire is reported by Liu et al. [16]. Furthermore, they have reported the improvement in power conversion efficiency using nanowire photovoltaic devices, primarily because of the enhanced spectral transmission of sunlight through the NW-CdS layer. The numerical analyses reported by Guo et al. [17] demonstrate the geometrical and morphological factors in the materials may modify the transmission spectra.

3.4 Photoluminescence (PL) studies

Room temperature photoluminescence spectra of CdO nanowire array measured in the visible region are shown in Fig. 5. PL spectrum shows band edge emission at 440 nm and green emission at 510 nm. The first peak attributed at 440 nm can be referred to the direct band transition (or band to band transition). The second peak at 520 nm is due to the exciton emission [12]. Green emission arises from the oxygen vacancy of CdO materials because of recombination of a photo generated hole in valence band with an electron in conduction band.

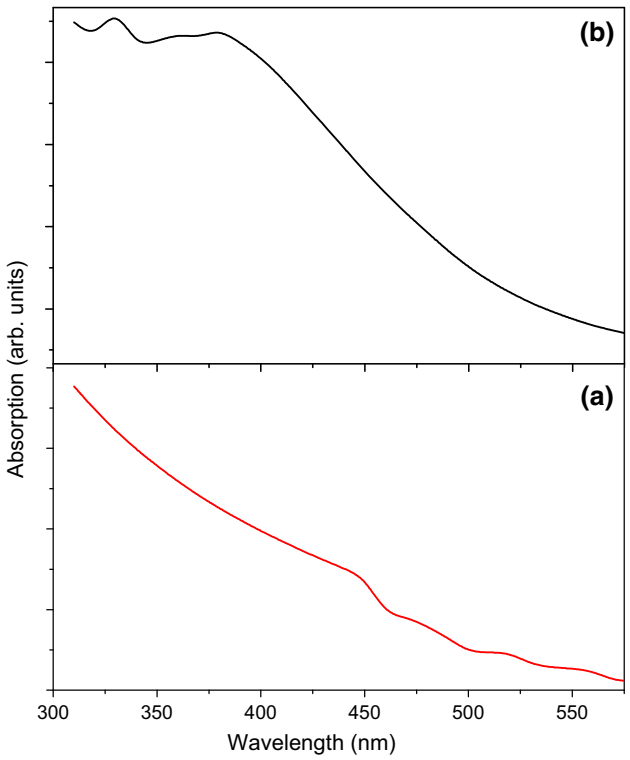

Fig. 3 Optical absorption spectra of **a** CdO nanowire array and **b** thin layer of CdO

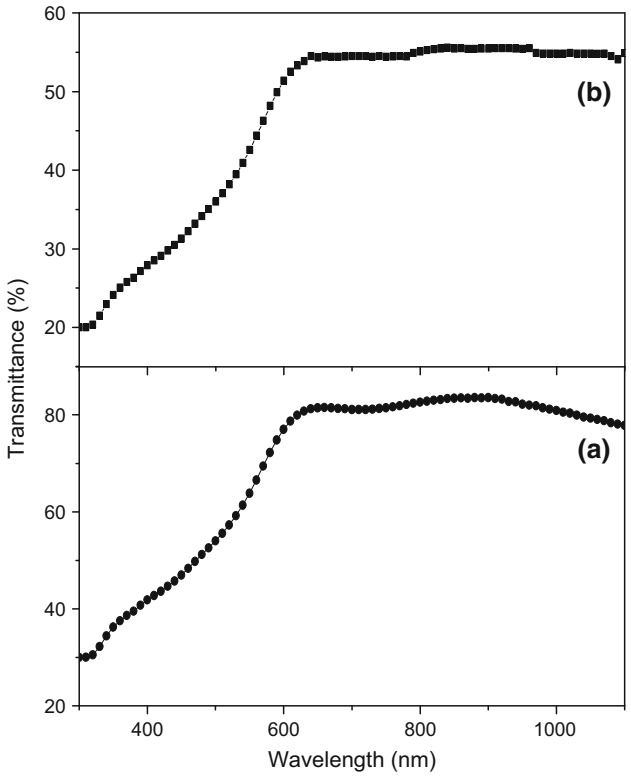

Fig. 4 Optical transmittance of CdO nanowire array **a** and thin layer of CdO **b**

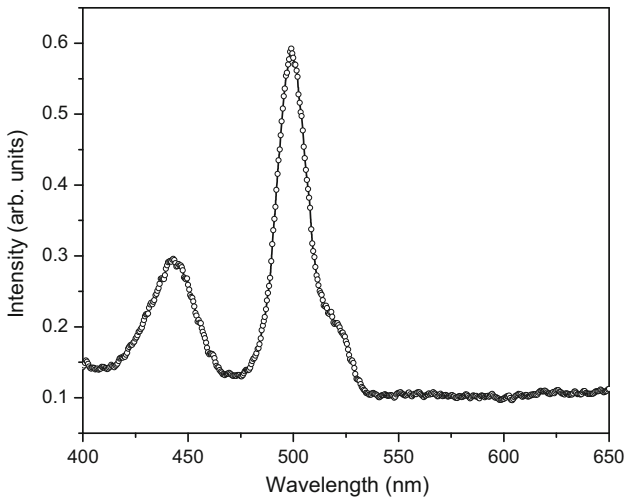

Fig. 5 Photoluminescence spectra of CdO nanowire array

4 Conclusions

A nanowire array and planar thin layer of CdO was successfully synthesized by galvanostatic electrodeposition technique. The uniform and vertically standing nanowire array of diameter ~50 nm and length ~2.5 μm was prepared. The free standing vertical nanowires were transferred to ITO substrates for device applications. The structural analysis revealed the growth of preferentially oriented nanowires along (200) plane as compare to the polycrystalline nature of planar thin layer grown under same conditions. A blue shift in the fundamental absorption edge, ~0.8 eV was observed for nanowire array. The average optical transmittance of ~80 % was measured to nanowire array in the visible region as compared to 55 % for planar thin layer. Photoluminescence spectrum shows band edge emission at 440 nm and green emission at 510 nm which can be attributed to direct band transition and exiton emission.

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