Solar Energy Materials & Solar Cells 94 (2010) 303–309

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Influence of thermal annealing on the structural and optical properties of CdSe nanoparticles

Umme Farva, Chinho Park*

School of Display and Chemical Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan 712-749, Republic of Korea

ARTICLE INFO

Article history:
Received 12 August 2008
Received in revised form
2 July 2009
Accepted 3 October 2009
Available online 4 November 2009

Keywords:
Cadmium selenide
Nanocrystal
Thermal annealing
X-ray diffraction (XRD)
Photoluminescence (PL) spectroscopy

ABSTRACT

CdSe nanocrystals of ~3–4 nm size have been synthesized by hot-injection method. The influence of thermal annealing in air- or N_2-atmosphere on the morphology and optoelectronic properties of synthesized CdSe nanoparticles has been elucidated. The CdSe nanoparticles showed phase transformation upon annealing in air at 350 °C from nanocrystalline sphalerite cubic (Zinc Blende, β-CdSe) structure to hexagonal (Wurtzite, α-CdSe) structure with a binding energy (Cd $3d_{5/2}$ peak) shift of 0.70 eV. Remarkable differences in the morphology and optoelectronic properties between air- and N_2- annealed CdSe nanoparticles were clearly observed. The intensity of PL emission increased substantially after annealing in air or N_2-atmosphere at 250 and 350 °C, respectively, indicating the improvement of crystallinity and surface passivation characteristics of the CdSe nanocrystals.

1. Introduction

Colloidal semiconductor nanocrystals have attracted much attention in recent years for their wide use in biological fluorescent labels [1], light-emitting diodes [2], lasers [3], thin film transistors [4], solar cells [5,6] and other nanoscale devices [7]. Cadmium selenide is a widely used A(II) B(VI) group semiconductor whose band gap (Eg=1.7 eV) lies in the solar energy spectrum [8] and has been studied as a photoanode in photoelectrochemical (PEC) cells [9–11] as well as an n-type active layer material in the low-cost high-performance bulk hetero-junction (BHJ) hybrid solar cells [12]. The CdSe nanocrystals are utilized in the BHJ hybrid solar cells to overcome the electron mobility limitations of the organic semiconductors involved and enhance the charge transfer rate. The power conversion efficiency of BHJ hybrid solar cells thus depends much on the quality of CdSe nanocrystals and its monodispersion characteristics in the polymer matrix.

Size-dependent emission is probably the most attractive property of CdSe nanocrystals, and by the one simple synthetic scheme, it is possible to synthesize variously sized CdSe nanocrystals that emit blue to red color with high purity. The intensity and line width of the photoluminescence (PL) spectra are important, because they are very sensitive to the nature of particle's surface, size, impurities and defects. Due to quantum size effect [13] the band gap of CdSe nanocrystal increases as its size decreases, and thus the emission color of the band-edge PL of the nanocrystals shifts continuously from red (centered at 650 nm) to blue (centered at 450 nm).

Hot-injection synthetic method provides great versatility for the preparation of highly luminescent colloidal CdSe nanocrystals with tunable size, shape, and surface passivation [14]. High degree of monodispersity can be achieved by the method without using the post-synthesis size-selective techniques [15]. Till date CdSe nanoparticles of spherical and non-spherical shapes, including hexagonal nanorods, nanowires, nanoneedles, dendrites, and tetrapods have been synthesized by hot-injection synthesis [16].

Phase transformation (e.g. β-CdSe→α-CdSe) of chemically synthesized II–VI semiconductors in the thin film state has been reported in the literature [17]. The thermal treatment induced polymorphic phase transition from a metastable cubic to a stable hexagonal phase has been reported in the thin film state [18] without showing any morphological changes, but for bulk CdSe nanopowder synthesized at an elevated temperature (> 80 °C), no such structural transitions are reported [19]. In the present study we elucidated the influence of thermal annealing (in air or N_2) on the morphological, structural and optical properties of the synthesized CdSe nanoparticles in detail. The band gap tuning of CdSe nanoparticles via thermal annealing was also investigated in air or N_2-atmosphere.

2. Experimental

All the chemicals used in this study were reagent grade and applied as-received. CdO was purchased from Junsei Chem. Co.,

* Corresponding author. Tel.: +82 53 810 2522; fax: +82 53 810 4631.
E-mail address: chpark@ynu.ac.kr (C. Park).

0927-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2009.10.003

and trioctylphosphine oxide (TOPO 99%), trioctylphosphine (TOP) and selenium powder were purchased from Aldrich. Hexylphosphonic acid (HPA) was purchased from Alfa Aesar Chemicals, and chloroform, hexane and methanol were purchased from Duksan Chemical Co.

The TOP/TOPO capped CdSe nanoparticles were synthesized by the slight modification of Peng and Peng method [20]. In a typical synthesis, CdO (0.514 g), HPA (0.2232 g) and TOPO (3.7768 g) were loaded in a two-neck reaction flask. The obtained mixture was heated to 320 °C under an argon atmosphere. At about 300 °C, reddish CdO powder was added to the flask, generating a homogeneous solution. The temperature of the solution was cooled naturally to 250 °C, and the stock solution of 0.237 g Se powder dissolved in 5 mL TOP was rapidly injected into the flask. After the injection, nanocrystals grew at 250 °C to reach ~3–4 nm size. The solution was cooled down to 50 °C, and then 15 mL of methanol was added to the flask to precipitate the nanoparticles, which were recovered by centrifugation at 4000 rpm. The precipitate was washed three times with methanol to remove the excess ligands and finally vacuum-dried to obtain the nanoparticles.

The CdSe nanoparticles were annealed at temperatures of 250, 350, and 450 °C for 30 min in open air or at temperatures of 250 and 350 °C in N_2-atmosphere to investigate the influence of thermal annealing on the optical and structural properties of synthesized CdSe nanoparticles.

X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectroscopy were utilized as major characterization tools to investigate the properties of nanocrystals. For TEM measurements, the nanoparticles were deposited onto 400-mesh copper Formvar/carbon grids and analyzed using a Philips CM 200 STEM operating at 200 kV. XRD analysis was carried out using a Rigaku D/Max-2000 powder diffractometer with CuK_α radiation operating at 40 kV and 100 mA. The room temperature PL spectra were obtained by a SPEX 750 M spectrometer using an argon laser (excitation wavelength=488 nm).

3. Results and discussion

Fig. 1(a–f) shows the TEM images of as-synthesized CdSe nanoparticles, air-annealed counterparts at 250, 350 and 450 °C, and N_2-annealed counterparts at 250 and 350 °C, respectively. Fig. 1(a) reveals that the particle size of synthesized CdSe nanoparticle is originally ~4 nm, and the particles are aggregated and agglomerated together in bunches which are not well dispersed. After the thermal treatment in both air and N_2 environment (Fig. 1b, c, e and f), however, the nanoparticles are clearly segregated and monodispersed with a little increase in the particle size to ~5 nm.

It is interesting to observe that, at the air-annealing temperature of 450 °C, the CdSe nanodots transform into nanorods of ~20 nm diameter with pyramidal ends on one side and flat ends on another side. This type of morphological change was not observed in annealed samples at or below 350 °C. Corresponding high resolution (HR) TEM images of each sample are depicted as insets in Fig. 1(a–f), which clearly show the close packing sequence with no dislocation in fringes. Lattice fringes were clearly observed, indicating synthesized nanoparticles were in single crystalline nature. In the case of sample (d) annealed at 450 °C in air, the HR-TEM image shows clear stacking of fringes having Wurtzite structure. Selected area electron diffraction pattern (SAED) was obtained for sample (d), clearly revealing well-defined rings of high crystallinity Wurtzite crystal structure. The observed SAED pattern can be indexed either to the hexagonal CdSe planes [(1 0 1), (1 1 0), (1 1 2) and (2 0 2)], cubic CdO plane (3 1 1) or hexagonal Cd plane (1 0 1), respectively [21]. It is noteworthy that increasing the annealing temperature in air leads to monodispersion of nanoparticles, phase change, and morphology change from quantum dots to nanorods. The CdSe nanoparticles annealed in N_2-atmosphere however did not show such substantial changes in the crystal morphology.

TEM-EDX measurement was made to characterize the chemical composition of sample (d), and it showed only the presence of Se and Cd without any impurities of other elements or products, also indicating the high purity of synthesized nanocrystals.

XRD patterns of CdSe nanoparticles (as-synthesized and annealed in air or N_2-atmosphere at various temperatures) are shown in Fig. 2. As-synthesized CdSe nanoparticles exhibited three diffraction peaks at $2\theta=25.2^\circ$, 41.9° and 49.7°, corresponding to the (1 1 1), (2 2 0), and (3 1 1) planes of metastable cubic (sphalerite) CdSe with the lattice constant, $\alpha=6.09$ Å [JCPDS No. 19-0191]. The observed d values of the diffraction peaks of CdSe nanoparticles and the relative intensities of the peaks were also compared to the standard d values, confirming the formation of metastable polycrystalline cubic phase of CdSe [22]. XRD patterns of annealed CdSe nanoparticles at 250 °C in both air- and N_2-atmosphere show the dominating cubic (1 1 1) peak as well as the appearance of the hexagonal phases (Figs. 2(i) and (ii)). After air annealing at higher temperatures of 350 and 450 °C, the diffraction peaks could be indexed as the (0 0 2), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes of Wurtzite hexagonal phase [JCPDS file cards 08-0459]. The XRD patterns of the sample air-annealed at 450 °C showed that the diffraction peaks become sharper with the decrease in the full width at half-maximum (FWHM) owing to the increase in the crystallinity and particle size along with the phase transformation. However, in the case of N_2-annealed sample at 350 °C, the (1 0 3) peak was less prominent than that of air–annealed sample, even though the phase change from cubic to hexagonal was identical.

The XPS spectra were observed to measure the chemical composition and surface properties of the annealed (in air- or N_2-atmosphere) and as-synthesized CdSe nanoparticles in detail, and the qualitative distinction observed from the XPS spectra of as-synthesized and annealed samples at 350 °C is illustrated in Fig. 3. Typical survey spectrum is shown in Fig. 3(i), mainly revealing the Cd and Se peaks from the nanoparticles. The C and O peaks were also observed, and they were believed to come from the surface capping layer (TOP/TOPO) of nanoparticles and from the adsorbed gaseous molecules. The full XPS spectra (Fig. 3(i); a–c) were identical in the number of peaks and their relative positions, except the oxygen peak intensity was higher in air-annealed samples (Fig. 3(i); b). High-resolution XPS spectra were taken for samples of as-synthesized and annealed at 350 °C under air- and N_2- environment, and the Cd 3d, Se 3d and O 1s spectra are shown in Fig. 3(ii–iv), respectively.

The Cd 3d features from as-synthesized CdSe nanoparticles consist of two main $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components at 405.35 and 412.0 eV, respectively (Fig. 3(ii)), which are close to the reported bulk values [23]. The Cd $3d_{5/2}$ peak was observed at 406.05 eV after air-annealing at 350 °C, shifted 0.70 eV towards higher binding energy, while it was found at 406.90 eV (1.55 eV shift towards higher binding energy) for samples annealed under N_2-atmosphere at the same temperature. These results clearly indicate the stronger bonding in the annealed samples, which is probably due to the tighter bonding interactions between atoms and surface passivation effect incurred by thermal annealing, as well as the structure change as evidenced by the XRD measurements [24].

Fig. 3(iii) shows the XPS spectra from Se 3d core level. In the case of as-synthesized CdSe nanoparticles, the Se 3d peak position was