Materials Letters 136 (2014) 67–70

Contents lists available at ScienceDirect

Materials Letters

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

White light emission from CdS/Si nanoheterostructure array

Yong Li [a,b], Shu Qing Yuan [a], Xin Jian Li [b,*]

[a] Department of Physics and Solar Energy Research Center, Pingdingshan University, Pingdingshan 467000, PR China
[b] Department of Physics and Laboratory of Material Physics, Zhengzhou University, Zhengzhou 450052, PR China

ARTICLE INFO

Article history:
Received 16 April 2014
Accepted 1 August 2014
Available online 8 August 2014

Keywords:
Nanocomposites
Luminescence
White light emission
CdS/Si nanoheterostructure array
Silicon nanoporous pillar array

ABSTRACT

A CdS/Si nanoheterostructure array (CdS/Si-NPA) is fabricated by depositing CdS nanocrystals (*nc*-CdS) on the silicon nanoporous pillar array (Si-NPA) through a chemical bath deposition method. White light emission from the CdS/Si-NPA is observed under the excitation of 350 nm, which originates from the color mixing of blue emission from Si-NPA and green and red emissions from *nc*-CdS. The chromaticity coordinate, correlative color temperature and color rendering index are (0.29, 0.36), 8226 K and 66.0, respectively. The chromaticity coordinates are insensitive to the excitation wavelength between 320 nm and 350 nm. It is suggested that the CdS/Si-NPA might be a kind of potential phosphor in the white light diode.

1. Introduction

In response to the demands for energy and the concerns of global warming and climate change, energy efficient and environmentally friendly solid state lighting, such as white light-emitting diodes, shows overwhelming promise in meeting the challenge of saving energy. Generally, white light emission is produced either based on discrete color mixing, color conversion, or direct white-light generation [1]. CdS is an important II–VI semiconductor material, with a band gap of 2.42 eV at room temperature, which can be used in electronic and optoelectronic devices, such as solar cells [2], light emitting diodes [3–5], laser [6], etc. CdS nanocrystals (*nc*-CdS) can be grown through many techniques [7,8], such as vacuum evaporation, sputtering, chemical bath deposition (CBD), etc. Among these techniques, the chemical bath deposition, which can be used to produce large area homogeneous films, is a simple, low-cost and safe technique [9]. Silicon nanoporous pillar array (Si-NPA) characterized by a micron-nanometer hierarchical structure can be used as functional substrates for constructing optoelectronic nanodevices [10]. In this paper, we fabricate a CdS/Si nanoheterostructure array (CdS/Si-NPA) through depositing *nc*-CdS on the Si-NPA using the CBD method. White light emission from CdS/Si-NPA is observed under the excitation of 350 nm and the origins are analyzed.

2. Experiments

Si-NPA was prepared by hydrothermally etching *p*-type (111) oriented, single crystal silicon (*sc*-Si) wafers in a solution of hydrofluoric acid containing ferric nitrate. Thedetail has been described previously [11]. CdS nanocrystals were synthesized and deposited on Si-NPA by a chemical bath deposition method. A mixture of cadmium chloride (0.03 mol l^{-1}), ammonia (15 ml, 18%) and de-ionized water (75 ml) was prepared. The mixture was placed into the bath fixed at 80 °C for 60 min with a magnetic agitation to homogenize the mixture. Soon afterwards 5 ml of ammonium chloride (0.1 mol l^{-1}) and 5 ml of thiourea (2.0 mol l^{-1}) were added to the mixture in turn. After 5 min, the Si-NPA was vertically placed into the solution to deposit CdS films for 40 min. The sample was taken out and washed thoroughly with de-ionization water and dried in the air atmosphere. As-grown CdS thin films were homogeneous, yellowish, and with good adherence to the Si-NPA. In order to obtain an improved quality, an annealing treatment at 500 °C was carried out in the high-purity (99.999%) argon atmosphere for 60 min.

The morphological and structural properties of CdS/Si-NPA were characterized by the field emission scanning electron microscopy (FE-SEM, JSM 6700F), a high-resolution transmission electron microscopy (HR-TEM, JEM-2100), and X-ray diffraction (XRD, Panalytical X'Pert Pro) using Cu$k\alpha$ as the X-ray source ($\lambda = 1.5046$ Å). The absorption of CdS/Si-NPA was obtained in a UV–vis–IR spectrophotometer (Shimadzu, UV-3150) with integrating sphere detector. The Raman spectrum was collected by a micro-Raman spectroscope (Renishaw RM2000). The room-temperature photoluminescence (PL) was measured using a double grating spectrofluorometer (HORIBA Join Yvon, FL3-22) with a Xe lamp as an excitation source.

* Corresponding author. Tel./fax: +86 371 67766629.
E-mail address: lixj@zzu.edu.cn (X. Jian Li).

http://dx.doi.org/10.1016/j.matlet.2014.08.001
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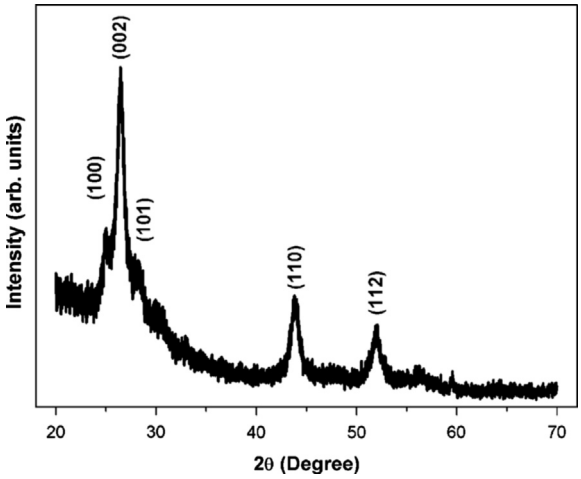

Fig. 1. XRD pattern of CdS/Si-NPA.

3. Results and discussions

As can be seen from Fig. 1, the XRD pattern of CdS/Si-NPA shows the hexagonal structure and gives a group of diffraction peaks corresponding to hexagonal CdS, such as (100), (002), (101), (110) and (112), which are located at 24.95°, 26.50°, 28.23°, 43.85° and 52.21°, respectively. Corresponding to the hexagonal structure of CdS, the XRD pattern has preferred orientation along the (002) direction. By analyzing the XRD data, a hexagonal lattice with cell parameters $a=4.218$ Å and $c=6.920$ Å is obtained [12]. Compared to the bulk CdS ($a=4.137$ Å and $c=6.714$ Å, JCPDS: 01-070-2553), the increase of the lattice constants a and c is observed, showing the existence of microstrain in the hexagonal CdS lattice originated from surface defects, such as vacancies and vacancy clusters [13,14]. According to Scherrer's formula [12] and the data corresponding to the (002) diffraction, the average size of *nc*-CdS is calculated to be ~19.3 nm. Due to the thickness of several hundred nanometers, the intensity for both the incident and emergent X-rays would be greatly attenuated. So the diffraction peaks of silicon cannot be observed in XRD pattern of CdS/Si-NPA.

Si-NPA is a silicon-based hierarchical structure characterized by its regular array of micro-sized, quasi-identical and highly porous silicon pillars [11]. As seen from Fig. 2(a), the fabricated CdS/Si-NPA maintains the morphological properties of Si-NPA and reveals that both the pillars and the valleys around the pillars are covered with *nc*-CdS and a continuous grain membrane of CdS is deposited on Si-NPA. It should be noted that some CdS particles with big sizes could be observed above the uniform CdS film. Considering that the average grain size evaluated by Scherrer's formula is only ~19.3 nm, these big particles should be the agglomerates of *nc*-CdS. From Fig. 2(b), we can observe many zones with distinct lattice fringes sized from ~5 nm to ~20 nm. Through measuring the fringe distances, these zones can be determined to be randomly and alternately dispersed by Si nanocrystals (*nc*-Si) and *nc*-CdS with different lattice orientations. Therefore, CdS/Si-NPA constructed by the *nc*-CdS and *nc*-Si is different to the conventional heterostructure, which possesses the larger interface. Due to the unique inherent morphological, electrical and optoelectronic properties this regular structure can improve charge separation and transport [15,16]. So, the CdS/Si-NPA might have emerged as one of the most promising candidates in the optoelectronic field.

Fig. 3 presents the Raman spectrum of CdS/Si-NPA under the excitation of 532 nm. Five optical vibrational Raman active modes located at ~302 cm^{-1}, ~393 cm^{-1}, ~606 cm^{-1}, ~694 cm^{-1} and ~909 cm^{-1} are observed. The intense and broad peaks at ~302 cm^{-1}, ~606 cm^{-1}, and ~909 cm^{-1} are assigned to the

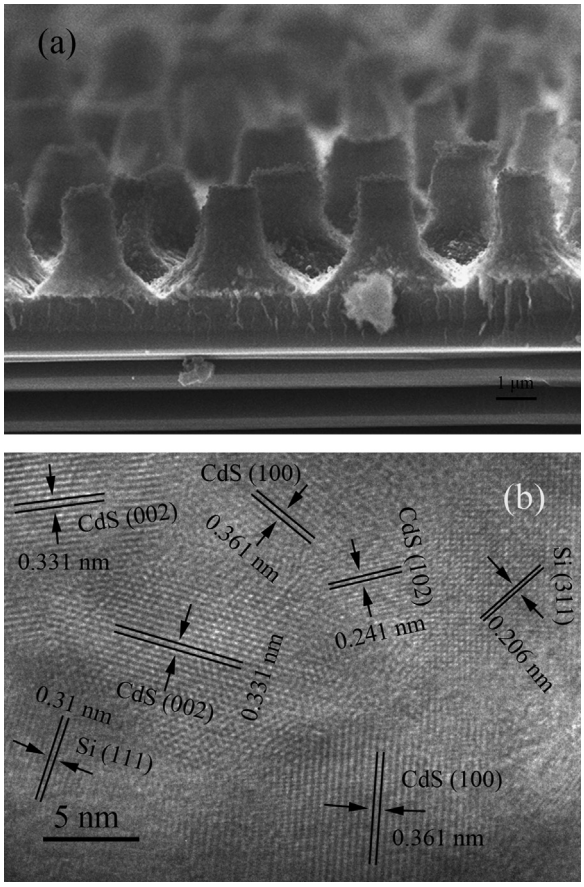

Fig. 2. (a) FE-SEM and (b) HR-TEM images of CdS/Si-NPA.

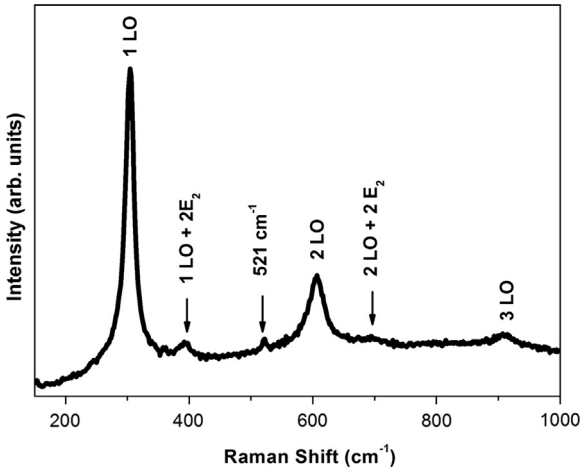

Fig. 3. Raman shift of CdS/Si-NPA under the excitation of 532 nm.

fundamental optical phonon mode (LO), the first overtone mode (2LO), and the second overtone mode (3LO) of CdS, respectively [17]. As compared to the bulk CdS (305 cm^{-1}) [18], the Raman peak of *nc*-CdS is downshifted and also shows asymmetric broadening. These features might be ascribed to the confinement of optical phonons in the *nc*-CdS [19]. The weak Raman peaks located at ~393 cm^{-1} and ~694 cm^{-1} result from multiphonon scattering [18], which are identified as those corresponding to the vibrational