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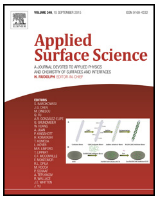

Temperature-dependent photoluminescence and mechanism of CdS thin film grown on Si nanoporous pillar array

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ABSTRACT

Si-based cadmium sulfide (CdS) is a prospective semiconductor system in constructing optoelectronic nanodevices, and this makes the study on the factors which may affect its optical and electrical properties be of special importance. Here we report that CdS thin film was grown on Si nanoporous pillar array (Si-NPA) by a chemical bath deposition method, and the luminescent properties of CdS/Si-NPA as well as its mechanism were studied by measuring and analyzing its temperature-dependent photoluminescence (PL) spectrum. The low-temperature measurement disclosed that the PL spectrum of CdS/Si-NPA could be decomposed into four emission bands, a blue band, a green band, a red band and an infrared band. The blue band was due to the luminescence from Si-NPA substrate, and the others originate from the CdS thin film. With temperature increasing, the peak energy, PL intensity and peak profile shape for the PL bands from CdS evolves differently. Through theoretical and fitting analyses, the origins of the green, red and infrared band are attributed to the near band-edge emission, the radiative recombination from surface defects to Cd vacancies and those to S interstitials, respectively. The cause of PL degradation is due to the thermal quenching process, a phonon-induced electron escape but with different activation energies. These results might provide useful information for optimizing the preparing parameters to promote the performance of Si-based CdS optoelectronic devices.

1. Introduction

In the past decade, the study on the preparing techniques and physical properties of cadmium sulfide (CdS) thin films has attracted much attention due to their potential applications in fabricating photovoltaic cells [1–4], light emitting diodes [5], laser diodes [6] and waveguide devices [7]. Accordingly a lot of preparing techniques, such as spray pyrolysis [8], close-spaced sublimation [9], chemical vapor deposition [10] and chemical bath deposition (CBD) [9] etc., have been developed for growing high-quality CdS thin films on different substrates. Among the methods, CBD deposition is thought to be most suitable for preparing CdS thin films with large-area uniformity, strong film-substrate adhesion and high reproducibility. Considering the leading position of single crystal silicon (*sc*-Si) possessed in large-scale device integration, the study on Si-based CdS systems is highly expected. Nevertheless, the large lattice (7%) and thermal mismatch (48%) existed between crystal Si and CdS make the direct growth of high-quality CdS thin films on *sc*-Si substrate be difficult [11,12], especially for the preparation by liquid chemical method such as CBD. Presently two routes are often adopted to abate the mismatches, one is through inserting an intermediate transition layer or layers [13], and the other is by growing Si (CdS) nanostructures on CdS (Si) bulk substrates [14,15], or even by growing Si (CdS) nanostructures on CdS (Si) nanostructures [6,16,17]. Si nanoporous pillar array (Si-NPA) is a Si hierarchical structure characterized by a regular array of micron-sized, quasi-identical and nanoporous silicon pillars, and has been proved to be with strong photoluminescence (PL) at room temperature and high light-absorption in wide spectral range [18]. The structural and physical features indicate that Si-NPA might be utilized as a functional template for assembling Si-based optoelectronic nanodevices, as has been illustrated in the fabrication of GaN/Si-NPA near-infrared light emitting diodes [19]. In the previous study, we have prepared a novel solar cell based on CdS/Si-NPA, but the final energy conversion efficiency is low [2]. It is clear that for CdS/Si-NPA solar cells, the CdS layer plays the roles as both the light absorber and the route for electron transport. This makes the control on the electro-optical properties of CdS film,

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which depends highly upon the defects or impurities formed during the CBD process, be a crucial factor for further promoting the device performance. Decided by the basic physics of luminescence, PL detection could be a sensitive and non-destructive optical technique for exploring optically activated recombination centers in semiconductors and can provide plentiful information about impurities and defect centers existed in material [20]. Especially, the temperature evolution of PL spectrum is very helpful for clarifying the origins of carrier recombination processes, including the luminescence from donor–acceptor transition [21], shallow trap states [22,23] and excitons [23]. Clearly, the clarification of these PL mechanisms can provide direct information for optimizing the preparing conditions to obtain high-quality CdS thin films.

In the paper, we report that a CdS/Si nanoheterostructure was prepared through growing CdS on Si-NPA by a CBD method followed by annealing treatments. The temperature evolution of the PL intensity and PL peak positions were investigated in a temperature range of 10–300 K. Based on the spectral results, the electronic structure and the defect states of as-grown CdS thin films were analyzed. A clear understanding of the mechanism will facilitate further design, optimization, and development of the optoelectronic devices based on CdS/Si-NPA.

2. Experiments

The Si-NPA substrates were prepared by hydrothermally etching (1 1 1)-oriented, boron-doped *sc*-Si wafers in the solution of hydrofluoric acid containing ferric nitrate. The description about the preparing process has been presented in detail elsewhere [18]. The CdS thin films were grown on Si-NPA by a CBD method. The CBD solution was a mixture solution of cadmium chloride, thiourea, ammonia and ammonia chloride with concentrations of 0.03, 0.1, 2 and 0.1 mol/l, respectively. In the CBD process, Si-NPA substrates were kept vertical in the bath, and the reaction mixture was stirred constantly with a magnetic agitator. The temperature for CBD deposition was fixed at 75 °C and the deposition process was lasted for 40 min. To obtain properly crystallized and stabilized CdS, an annealing treatment was carried out at 500 °C in high-purity N_2 atmosphere for 20 min.

The crystal structure and surface morphology of CdS/Si-NPA were characterized by an X-ray diffractometer (XRD, Panalytical X'Pert Pro) and a field emission scanning electron microscope (FE-SEM, JSM 6700F). The PL spectra were measured at different temperatures by using a double grating spectrofluorometer (HORIBA, FL-3-22) equipped with a closed-cycle helium cryostat (Jannis CCS-100) and a digital temperature controller (LakeShore-325) to provide continuous temperature variation from 10 to 300 K. The excitation wavelength was set as 350 nm, with a bandpass of 5 nm. A long-pass filter centered at 400 nm was used to eliminate the stray light and the second order diffraction light.

3. Results and discussion

The XRD pattern of CdS/Si-NPA is shown in Fig. 1, where altogether eight diffraction peaks are observed. These diffraction peaks are respectively indexed to the reflections from (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 3) family planes of wurtzite CdS (JCPDS card: No. 41-1049), a preferable crystal phase of CdS for solar cell applications [24]. No diffraction peaks of crystal Si from Si-NPA substrate were observed, inferring that the X-ray diffraction from Si-NPA substrate is very weak after penetrating the deposited CdS film. According to Scherrer's formula [25] and based on the XRD data, the average grain size in as-grown CdS thin film was evaluated to be ~21 nm. This indicates that the CdS thin film is composed of CdS nanocrystallites (*nc*-CdS).

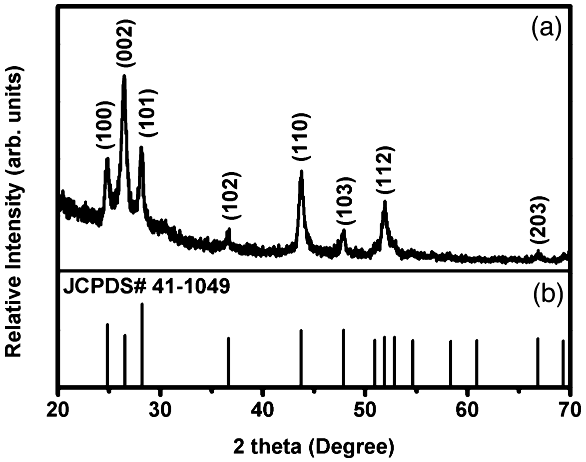

Fig. 1. (a) The XRD pattern of CdS/Si-NPA. (b) The standard XRD pattern of hexagonal wurtzite CdS.

As shown in Fig. 2(a) and illustrated previously [18], Si-NPA possesses a hierarchical structure characterized by a regular array composed of micron-sized, quasi-identical and nanoporous silicon pillars. The typical surface morphology of CdS/Si-NPA is given in Fig. 2(b) and Fig. 2(c). It is found that after the CBD process, both the pillars and the valleys surrounded the pillars were covered with a continuous and highly packed CdS grain membrane, but the morphological feature (the regular array) of Si-NPA is inherited by CdS/Si-NPA.

The temperature evolution of the PL spectrum of CdS/Si-NPA is shown in Fig. 3(a). Here the selected PL spectra were measured at 10, 20, 40, 60, 70, 90, 100, 130, 200, and 300 K, respectively. Obviously the PL spectrum changed gradually but greatly with temperature. The changes include the PL peak positions, the relative strength of the peak intensities amongst the emission bands for each spectrum, and the peak shape profiles. To determine the basic components of the PL spectrum of CdS/Si-NPA, the spectrum measured at 10 K is re-depicted in Fig. 3(b) (solid curve). Obviously, from short to long wavelength direction, the PL spectrum can be well resolved into four PL bands, a blue band (B band), a green band (G band), a red band (R band) and an infrared band (IR band), with the peak positions locating at ~2.84 eV (436 nm), 2.20 eV (563 nm), 1.80 eV (688 nm) and 1.53 eV (810 nm), respectively [26]. Here all the peak energies were obtained by performing a Gaussian fitting process accordingly. From Fig. 3(a), it is easy to find that with temperature increasing, the intensities of all the PL bands decreased gradually, accompanied with an obvious broadening of their full width at half maximum (FHWM). Deducing from the preparation process and the microstructure of CdS/Si-NPA, the four PL bands might originate from the CdS thin film, the CdS-Si-NPA interface or the underneath Si-NPA substrate. To clarify the role played by Si-NPA substrate in the luminescence, a Si-NPA sample was annealed with the same conditions as that for CdS/Si-NPA (at 500 °C for 20 min in high-purity N_2 atmosphere), and the PL spectrum was compared with that of CdS/Si-NPA, as shown by the dashed curve in Fig. 3(b). Clearly, the annealed Si-NPA shows only a broad blue PL band, and both its peak energy and peak shape profile are almost identical to those of CdS/Si-NPA. So it is reasonable to attribute B band from CdS/Si-NPA to the emission from Si-NPA substrate [18]. Furthermore, the peak position of B band remains almost unchanged at different measuring temperatures (Fig. 3(a)).

To elucidate the origins of the other emission bands, the temperature evolution of the peak energy and peak intensity for G, R and IR bands are depicted in Fig. 4. With temperature increasing, the peak energies of the three PL bands show different evolution trends (Fig. 4(a) and (b)), yet all the peak intensities decrease