Journal of Alloys and Compounds 595 (2014) 46–50

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Controllable deposition of cadmium oxide and hydroxide nanostructures on silicon using a hydrothermal method

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ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 27 December 2013
Accepted 7 January 2014
Available online 18 January 2014

Keywords:
CdO
$Cd(OH)_2$
Hydrothermal method
Photoluminescence
Nanostructure

ABSTRACT

We report on the growth of CdO and $Cd(OH)_2$ nanostructures with different morphologies on Si substrates by using a hydrothermal method. Structural and optical investigations showed that the shape and phase could be modified through the growth time and the concentration in the solution. The formation of CdO was dominated during the early stage of growth and at a low source concentration, while that of $Cd(OH)_2$ was dominated at the later stage of growth with a higher source molar concentration. And the mechanism was explained by the thermodynamically favorable reaction. Our results indicate that the morphology and crystalline phases of CdO and $Cd(OH)_2$ nanostructures can be controlled on the Si substrates for various applications.

1. Introduction

CdO and $Cd(OH)_2$ nanostructures (Cd-OHNS) have received great attention for optoelectronic applications including light-emitting diodes, solar cells, and phototransistors, and for sensors, diodes, and cathode electrodes for batteries [1–4]. CdO is regarded as an important *n*-type semiconductor with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV, depending on the vacancies and crystal structure [5,6]. $Cd(OH)_2$ is also regarded as an important material that can be used as a converting precursor for the fabrication of CdO nanostructures [7], and as a wide band gap semiconductor with high electrical conductivity [8,9]. Therefore, many researchers have reported on the fabrication of CdO or $Cd(OH)_2$ nanostructures through various methods including the template-assisted method [10], sol–gel method [11], and solvothermal method [12]. However, few have been reported for the controlled fabrication of Cd-OHNSs, especially using the hydrothermal method [13], even though this method has many advantages of low temperature process which make it favorable for the integration and in situ fabrication of various devices [14]. Furthermore, the methods reported focused on the fabrication of nanopowders [11–13], which are not easy to apply to various devices, and the shape and position of the nanostructures are difficult to control. For more compatible applications of Cd-OHNSs to other devices, the fabrication process should be controllable and the nanostructures could be fabricated on a range of substrates. We report on the controllable fabrication of Cd-OHNSs on a silicon (Si) substrate using a two-step hydrothermal method.

2. Experimental details

2.1. Experimental

Cd-OHNSs with different shapes were fabricated on *n*-Si (100) substrates using a two-step hydrothermal method, involving the formation of a CdO seed layer and main growth of Cd-OHNS layer. The Si substrate was cleaned by using acetone, methanol, buffered oxide etch, and deionized (DI) water. A CdO seed layer was formed on the cleaned Si substrate by dipping it into 80 mM of cadmium acetate [$Cd(CH_3COO)_2$, 99.995%, Sigma–Aldrich] dissolved in ethanol solution followed by drying at 120 °C for 5 min in the oven. The main growth of the Cd-OHNS layers were processed by placing the seed layer-grown substrate into a mixed solution of cadmium nitrate [$Cd(NO_3)_2$, 98.0%, Sigma–Aldrich] and hexamethylenetetramine (HMT, 99.0%, Kanto Chemical) in a mixed solution of DI water and ethylene glycol (3:1) at 150 °C. At a solution temperature lower than 130 °C, no Cd-OHNS was formed on the substrate. The amount of cadmium nitrate and HMT for solution of main growth was varied from 20 to 200 mM. At a solution temperature above 70 °C, the solution started to become cloudy, indicating that a chemical reaction had started. After the deposition, the samples were cleaned in flowing DI water for 5 min.

2.2. Characterizations

A structural characterization of the Cd-OHNSs was performed by field emission-scanning electron microscopy (FE-SEM, Hitachi, S-4800) operating at 20 kV, field emission-transmission electron microscopy (FE-TEM, Hitachi, HF-3300) operating at 200 kV, and X-ray diffraction (XRD, PANalytical, MPD for thin film) using Cu Kα radiation. The chemical composition of the Cd-OHNSs was measured by energy

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http://dx.doi.org/10.1016/j.jallcom.2014.01.045
0925-8388/

dispersive X-ray spectroscopy (EDS, Hitachi, S-4800) attached to the FE-SEM and FE-TEM. The optical properties of the Cd-OHNSs were studied using photoluminescence (PL) spectra, which were measured using a 24 mW power 325 nm continuous He–Cd laser (Kimmon Koha) at room temperature. The laser was focused onto the sample's surface using an objective lens. The excitation area was estimated to be approximately 400 μm in diameter.

3. Results and discussion

Fig. 1 shows FE-SEM images of the Cd-OHNS layers grown in a solution of 120 mM of HMT and cadmium nitrate for various growth times. The Cd-OHNS layers were grown on the seed layer-grown Si (100) substrates. Without the seed layer, no deposits was observed, even at a longer growth time (not shown here). In the early stage (shorter than 1 h), no substance formed on the substrate. As the growth time increased to 2 h, nanowires (NWs) were formed. When the growth time was increases further, three-dimensional (3D) crystallites formed, and the NWs disappeared gradually. The details about the formation mechanism of these structures are discussed in later section based on the structural and optical investigations.

Fig. 2 shows the shape evolution of the Cd-OHNS layers with variation of the source molar content from 20 to 200 mM. The growth time and the solution temperature were kept constant at 2 h and 150 °C, respectively. When the molar content was 20 mM, the Cd-OHNS layer was composed of short one-dimensional (1D) NWs. As the source molar content increased to 120 mM, the length and the diameter of the NWs increased gradually. When the source molar content increased to 160 mM, both of 3D and 1D nanostructures started to appear. As the source molar concentration increase to 200 mM, the 1D NWs disappeared completely and only 3D tapered structures were observed on the surface. As the cadmium nitrate and HMT molar concentration increased, the Cd-OHNS showed shape evolution from 1D NW shapes to 3D tapered structures. To investigate the composition of the deposited 3D tapered shapes, the EDS was measured at a selected area of the sample grown with 200 mM solution, as shown in Fig. 3. The EDS pattern shows that the Cd and O elements are contained in the 3D Cd-OHNS. The peak noted Pt corresponds to the coating material for SEM measurement. Other impurities, such as a carbon-related complex incorporated from the sources, were not observed.

Fig. 4 shows TEM images for the 120 mM sample. The HR-TEM images indicate that the 1D NW structure in the sample is a single-crystalline structure with well-defined atomic layers. The atomic spacing was estimated to be 0.27 nm, corresponding to the (111) plane of CdO. CdO is a rock-salt crystal structure with a lattice constant of 4.695 Å. The EDS result for the structure showed mainly Cd-related compounds, as shown in Fig. 4(b). Based on the HR-TEM and EDS results the 1D NW in the 120 mM sample could be identified as crystalline CdO. Because the surface energy of the polar (111) plane is higher than that of the nonpolar (100) plane,

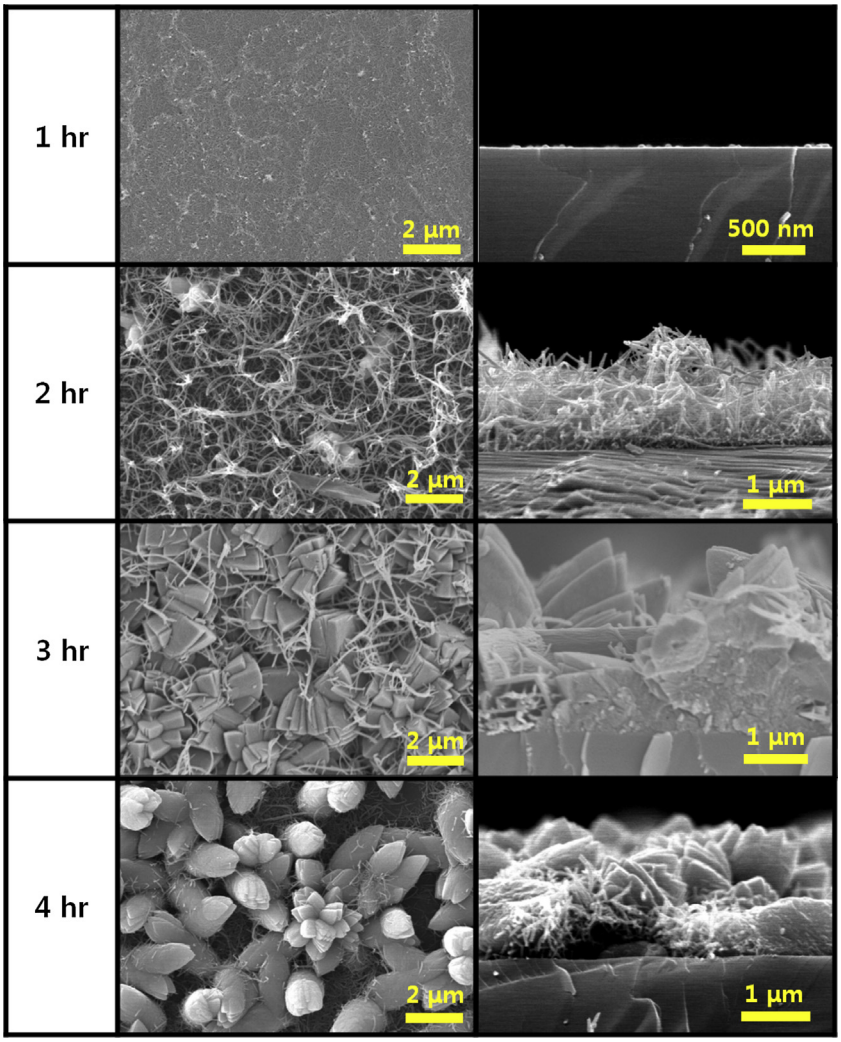

Fig. 1. FE-SEM images of Cd-OHNS layers grown on *n*-Si (100) substrates with growth time.