Journal of Crystal Growth 312 (2010) 685–691

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Synthesis of nanostructures of copper compounds and their hybridisation with titanate nanosheets

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ARTICLE INFO

Article history:
Received 23 October 2009
Received in revised form
7 December 2009
Accepted 9 December 2009
Communicated by K. Nakajima
Available online 16 December 2009

Keywords:
A1. Nanostructures
A2. Growth from solution
A2. Seed crystals
B1. Copper compounds
B1. Titanate nanosheets.

ABSTRACT

Our results in the field of adopting the chemical bath deposition method (CBD) for the deposition of the nanostructures of copper compounds are presented in this work. The deposition of copper compounds by means of the CBD method was carried out at the water solution of copper nitrate (acetate) salts and hexamethylenetetramine. There are two distinct periods in the deposition of copper compounds in the same bath. At the shorter deposition time the good quality nanocrystals of the copper hydroxy nitrate (acetate) salts with a different morphology are obtained. Decomposition of the copper salts to the CuO in the water bath can be observed after several hours of the copper hydroxy salts deposition. The SEM images and the XRD patterns of the CuO layer, which was produced by decomposition of copper hydroxy salts by the CBD method, show a morphology and texture different from the CuO layer prepared by thermal decomposition of the deposited copper hydroxy salts at an elevated temperature.

It has been suggested that the main force in decomposition of copper hydroxy salts to CuO in the course of CBD process may be related with a strain, which exists between the CuO nanoparticles on the modified glass substrate and the deposited copper hydroxy salt. The decomposition reaction of copper hydroxy salts in the solid phase may be accelerated by a strain. The influence of the strain on the morphology of CuO nanostructures is demonstrated on the basis of the basic copper nitrate salt hybridised with titanate nanosheets.

1. Introduction

The synthesis of nanostructured thin films of a semiconductor and metal oxides has attracted an increasing attention in recent years due to their potentially superior electronic and optical properties compared with those of the corresponding bulk materials. The zinc oxide and the copper compound have attracted much attention, because of their versatile applications in electronic, catalytic and electrochemical systems, and nanotechnology [1–4]. Compared with spherical nanoparticles or molecular precursors studied to date, the lamellar nanosheets and nanorods are advantageous as a building block. Specific physical properties of the zinc oxide and the copper compound can be expected when particles are not spherical but elongated in one dimension (nanorods) or two dimensions (platelets).

Among many different methods available for depositing films of semiconductors and metal oxides, the chemical bath deposition (CBD) is conceptually the simplest [5]. The CBD refers to deposition in a solution (usually water), where the required deposit is both chemically generated and deposited in the same bath. The main cause of interest in this technique is the fact that the crystals in CBD films are often very small. Taking into consideration the current interest in nanoparticles, the CBD is an excellent technique of depositing nanocrystalline films. Up to now, the ZnO nanorods array was deposited on the ITO glass by means of the CBD method. The coupling of ZnO nanorods with other semiconducting organic or inorganic materials has also received special attention as an alternative tool for tuning the ZnO electronic structure and functionality [6–8].

The oxides of transition metals such as Zn and Cu represent one of the most diverse classes of materials with important size-dependent optical, electronic and other physical properties, and wide range applications. The CuO as a p-type semiconductor with a narrow band gap (1.2 eV) is a candidate material for photothermal and photoconductive applications [9]. Additionally, it is an effective catalyst and a useful component in the fabrication of sensors [3] and magnetic storage media [10]. Recently, new nanostructures of the CuO were synthesised using the wet chemical approach. The synthesis of the sheaf-like CuO nanostructure in the hydrothermal conditions for their application in the lithium-ion battery and the flower-like CuO nanostructure via a simple hydrolysis process for photocatalytic performance was presented in the literature [11,12]. The chemical reagents in both cases were $Cu(NO_3)_2 \cdot 3H_2O$ and hexamethylenetetramine.

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0022-0248/$ - see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jcrysgro.2009.12.022

Our results in the field of the nanostructures synthesis of copper compounds by applying the chemical bath deposition method (CBD) are presented in this work. When using the CBD method the layers of metal oxide nanoparticles on the solid substrate as seeds of the heterogeneous nucleation and growth are necessary (modified glass substrate). In the case of ZnO nanorods array deposition, the ITO glass substrate modified with the ZnO nanoparticles layer is obtained through the sol–gel process followed by subsequent calcinations. In our analysis the nanoparticle layers of the CuO on the glass support were obtained by calcinations of the nanocomposite of the (2-hydroxypropyl)-cellulose with the CuO nanoparticles.

First, the nanostructures of copper compounds layers obtained by the CBD deposition method will be presented. In the next step, the method and effect of the hybridisation of the copper compound with titanate nanosheets will be shown.

2. Experimental details

Materials: copper(II) nitrate trihydrate, puriss. p.a., 99%, copper(II) acetate monohydrate, puriss. p.a., ≥ 99.0%, (2-hydroxypropyl)cellulose (HPC), $M_w \sim 100{,}000$, hexamethylentetramine $(CH_2)_6N_4$ (HMTA), ACS Reagent ≥ 99.0%, 1-propanol, ACS reagent ≥ 99.5%. All reagents were purchased from the Sigma–Aldrich and used without further purification.

2.1. Sample preparation

2.1.1. The copper compound deposition

The deposition of copper compounds on the modified glass substrate was carried out by means of the chemical bath deposition method described in the Ref. [5]. The procedure consists of two steps: (1) formation of the CuO nanoparticles on glass substrates as seeds of the heterogeneous nucleation (modified glass substrate) and (2) heterogenous nucleation and growth of the copper compound on the modified glass substrate in the aqueous solution of the copper nitrate or the copper acetate and hexamethylenetetramine.

(1) The modified glass substrates (2.5 cm × 7.5 cm) by CuO nanoparticles were obtained by adopting the sol–gel process in (2-hydroxypropyl)cellulose presence [13]. The 0.200 g (1.0 mmol) of copper acetate monohydrate (CuAc) with 0.400 g of (2-hydroxypropyl)cellulose (HPC) were dissolved in 9.198 g (11.50 ml) n-propanol with addition of 0.202 g (2.0 mmol) triethylamine (TEA). The glass plates with spacers (50 μm) were covered by a sol solution. The gelation and drying in the air conditions (25 °C, 60% humidity) proceeded. The obtained xerogel layers were annealed at 160 °C for 10 h leading to the nanocomposite CuO/HPC formation with CuO content—17 wt%. The CuO nanoprticles layer was prepared by calcination of the CuO/HPC nanocomposite at 500 °C for 2 h. The surface density (τ_{CuO}) of obtained glass substrates modified by the CuO nanoparticles layer was calculated by assuming 100% conversion of the CuAc to the CuO and sol density—0.8 g/ml. The CuO with surface density 0.3 g/m^2 is obtained for specified conditions: thickness of the sol layer—50 μm, content of the copper acetate in the sol—2 wt%, and density of the sol—0.8 g/ml.

(2) The heterogeneous nucleation of the copper compound and growth of crystals were carried out in a sealed bottle by immersing the modified glass substrate in the aqueous solution (100 ml) containing $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 M) and hexamethylenetetramine $(CH_2)_6N_4$ (0.05 M). The sealed bottle was kept at 90 °C in a drying oven. The immersion time necessary for the deposition was typically over 2 h. The deposition using an aqueous solution of the copper acetate salt $Cu_2(CH_3COO)_2 \cdot H_2O$ was carried out in the same conditions.

2.1.2. Synthesis of titanate nanosheets

The synthesis of titanate nanosheets has been already described [14]. The methacrylic acid (MAA) 0.33 g (3.83 mmol) was directly added into (tetra-isopropoxy)titanate (TIPT) 2.17 g (7.63 mmol) in the room temperature and the nitrogen atmosphere. The formed MAA/TIPT complex is introduced to 50 g of the hydrogen peroxide solution with 15% concentration and mixed intensively for about 4 h in the air and in the room temperature. The process of hydrolysis and mineralisation of MAA/TIPT complex is accompanied by a considerable rejection of gas products. Due to the exothermic reaction, cooling the reaction mixture is recommended. Poly(ethylene glycol) (0.1 ml, M=300) was used as a protective agent counteracting the sedimentation of the mineralisation product. The final product (50 ml) is a suspension of the colloidal inorganic phase of the oxotitanium compound in the water solution and it is called a hydrosol. The hydrosol was shaken vigorously with the tetramethylammonium hydroxide (1.8 ml 25% water solution), which produced a translucent colloidal suspension. The titanate nanosheets as a precipitate were obtained by adding an excess amount of 2-propanol to the solution, separated by the centrifugal separation, then washed with 2-propanol and finally dried in the vacuum.

2.1.3. The hybridisation of the copper hydroxy nitrate layer with titanate nanosheets

The hybridisation of the copper hydroxy nitrate was carried out by impregnating the copper hydroxy nitrate layer using a solution of HPC (0.476 g) in the deionised water (5.0 ml) and 0.025 g or 0.114 g titanate nanosheets. The surface density of titanate nanosheets after impregnation was calculated from the amount and concentration of the solution of HPC and titanate nanosheets in the water. The layers after impregnation were air dried and next annealed at 180 °C during 1 h. The ternary composite after impregnation composed of the copper hydroxy nitrate, titanate nanosheets and the HPC was calcinated at temperatures 500–550 °C, at which the organic component of the hybrid-HPC is transformed into a gaseous product and the copper hydroxy nitrate is decomposed to the copper oxide. The titanate nanosheets transform to TiO_2 nanocrystals at 500 °C [15]. Two samples of hybrids CuO/TiO_2 were prepared by using two values of the surface density (τ) of titanate nanosheets (TN) named CuO/TiO_2 I (τ_{TN}=0.2 g/m^2) and CuO/TiO_2 II (τ_{TN}=1.1 g/m^2).

2.2. Sample characterisation

The X-ray diffraction patterns of samples were obtained using the X-ray Siemens D 5000 X-ray diffractometer, which irradiated the samples with the monochromatic CuK$_\alpha$-doublet (40 kV, 30 mA). The diffraction curve was recorded in 2θ-steps of 0.03° with the counting time of 3 s per step for all samples. SEM images were obtained on the scanning electron microscope Hitachi S3000 equipped with the energy dispersive X-ray spectrometer (EDX). The Raman spectra investigations were performed using a dispersive spectrometer, model Jobin–Yvon T 64000, equipped with a confocal microscope. They were measured at 293 °K using the argon-ion laser wavelength λ=514.5 nm.