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The impacts of growth temperature on morphologies, compositions and optical properties of Mg-doped ZnO nanomaterials by chemical vapor deposition

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ABSTRACT

The Mg-doped ZnO ($Zn_{1-x}Mg_xO$) nanomaterials with different morphologies of nanoparticles, partially opened nanowire-on-spherical shells, hemispheric shells and chain-like nanoparticles were synthesized at 750, 850, 900 and 1000 °C by a simple chemical vapor deposition. The energy dispersive X-ray (EDX) measurements indicate that Mg content increases from 2.87 at.% to 5.01 at.% with the increase of growth temperature from 750 to 1000 °C. The measurement results of X-ray diffraction (XRD) show that the (002) peaks of $Zn_{1-x}Mg_xO$ nanomaterials shift to higher diffraction angle with the increase of Mg content, implying that Mg^{2+} is substituted into Zn^{2+} site. The absorption spectra at room temperature exhibit that the band gap of the Mg-doped ZnO nanomaterials increases with the Mg concentration, illustrating that the modulation of band gap is caused by Mg addition. The PL measurements show that UV peak from $Zn_{1-x}Mg_xO$ nanomaterials is shifted towards lower wavelength side (blue shift) from 381 nm to 372 nm with the increase of the Mg dopant content. The room-temperature Raman spectra show that the crystal quality of the $Zn_{1-x}Mg_xO$ nanomaterials is improved with the increase of growth temperature, and the Mg dopants do not decrease the crystal quality of ZnO nanomaterials.

1. Introduction

ZnO is a wide-band gap semiconductor with a direct band gap energy of 3.37 eV and exciton bounding energy of 60 meV [1], which is much larger than that of ZnSe (22 meV) and GaN (25 meV). In this regard, ZnO has attracted considerable attention because of great potential application in optoelectronic devices, especially in ultraviolet lasing and laser diodes [2]. ZnO at nanoscale exhibits some novel physical properties which are substantially different from their bulk counterparts. To enhance the optical and electrical properties of ZnO, doping with suitable transition elements has been preferred [3]. Doping of Mg in ZnO permits the band gap to be tailored and decrease the oxygen vacancies and electron density [4]. So, Mg doping will have considerable influence on the optical properties of ZnO and it paves the way to obtain tunable optical and electrical properties.

Recently, many researchers have reported the formation of $Zn_{1-x}Mg_xO$ nanostructures with different methods such as the metal–organic vapor phase deposition [5–7], pulsed laser deposition [8], and thermal evaporation [9–13]. However, there are few reports on Mg-doped ZnO nanomaterials deposited on quartz glass substrate by chemical vapor deposition technique. In comparison with other equipments, the chemical vapor deposition technique has many advantages in the preparation of $Zn_{1-x}Mg_xO$ nanomaterials, such as low cost and high growth temperature. The high growth temperature can produce the high crystal quality of $Zn_{1-x}Mg_xO$ nanomaterials and make Mg dopant diffuse well into the base compound. Quartz glass substrate has good light permeability and a potential application for the window material for solar cells. Therefore, it is necessary to investigate the fabrication of $Zn_{1-x}Mg_xO$ nanomaterials on quartz glass substrate.

In this paper, we report that the different morphologies of Mg-doped ZnO nanomaterials on transparent quartz glass substrate were synthesized by a simple chemical vapor deposition technique. The results indicate that the evaporation temperature plays a crucial role on controlling the morphologies, compositions and optical properties of $Zn_{1-x}Mg_xO$ nanomaterials.

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2. Experimental details

The mixture of pure Zn powder (99.99%) and Mg block (99.99%) in a weight ratio of 4:1 was placed in an alumina crucible and melted at 800 °C in a furnace under air ambient. Then the melt was stirred using an alumina rod. After the furnace was cool down to room temperature, the Zn and Mg alloys were divided into many small blocks used as the source materials to synthesize $Zn_{1-x}Mg_xO$ nanomaterials. Energy dispersive X-ray (EDX) analysis confirmed that the molar ratio of Mg in the Zn and Mg alloys source material is 13.26%. $Zn_{1-x}Mg_xO$ nanomaterials were synthesized by chemical vapor deposition method in a horizontal tube furnace. The experimental setup is schematically demonstrated in Fig. 1(a). The Zn and Mg alloys were loaded into a quartz boat placed at the end of a one-end sealed quartz tube with 2 cm in diameter. Quartz substrates were placed about 20 cm away from the source material to receive the products. Then the quartz tube was inserted into the horizontal tube furnace and made the sealed end at the center of the furnace tube. After that, the tube furnace was evacuated by using a mechanical rotary pump to remove the residual oxygen and was heated to appropriate temperatures of 750, 850, 900 and 1000 °C, respectively, at a rate of 15 °C/min. As soon as it reached the desired temperature, we stopped the evacuation of the mechanical rotary pump, keep the system for 2 min at the growth temperature, then introduced the mixed-gas of argon and oxygen with a ratio of 2:1 into the furnace system, at the same time, we open the vent valve to make the mixed-gas naturally flow out. The growth time is 50 min. Prior to the growth, the quartz substrate was treated with ethanol in an ultrasonic bath to remove surface contamination and etched in HCl solution at 80 °C for 10 min, and then rinsed in deionized water and lown dry using high-purity nitrogen. The yellowish powder on the quartz substrate could be obtained after the furnace was cooled to room temperature naturally. As a comparison, the pure ZnO nanoparticles without Mg dopant were also synthesized at 750 °C under the same condition, the pure Zn metal was used as source material.

The morphology and structure of the $Zn_{1-x}Mg_xO$ nanostructures were characterized using a field emission scanning electron microscope (FE-SEM; Philips XL30FEG) with an accelerating voltage of 5 kV, X-ray diffraction (XRD) measurement was performed by using a RigakuO/max-RA X-ray diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.15418$ nm). Energy dispersive X-ray (EDX) analysis was also performed during the FE-SEM observation. The micro-Raman in the backscattering geometry and photoluminescence (PL) spectra were recorded at room temperature by a Jobin Yvon LabRAM HR800UV micro-Raman system under an Ar^+ (514.5 nm) and a He–Cd (325.0 nm) laser excitation, respectively. Optical absorption spectra were recorded by using a UV-3101PC spectrometer.

3. Results and discussions

Fig. 2(a)–(c), (f) and (g) shows the typical FE-SEM images of the prepared pure ZnO nanoparticles at 750 °C and $Zn_{1-x}Mg_xO$ nanomaterials at 750, 850, 900 1000 °C for 50 min, respectively. When the growth temperature is at 750 °C, ZnO and $Zn_{1-x}Mg_xO$ exhibit nanoparticles, their average diameters are about 0.05 and 1.5 μm. With the increase of growth temperature, the products are evolved into partially opened nanowire-on-spherical shells at 850 °C, hemispheric shells at 900 °C and chain-like nanoparticles at 1000 °C, and their average diameters are bout 5, 7 and 0.05 μm, respectively. To clearly indicate the partially opened nanowire-on-spherical shells at 850 °C, the magnified SEM images for the outside and internal structures were shown in Fig. 2(d) and (e). It will be found that the ZnO nanowires are formed on the outside and internal surfaces, the nanowires are 15 nm in diameter and 400 nm in the length.

EDX measurements have been carried out on the compositions of the synthesized $Zn_{1-x}Mg_xO$ nanomaterials, as shown in Fig. 3. The results indicate that the synthesized $Zn_{1-x}Mg_xO$ nanomaterials are composed of Zn, Mg and O elements, the signal of Si originates from the quartz glass substrate, as shown in Fig. 3(b)–(e). Moreover, no Mg element was detected in pure ZnO nanoparticle at 750 °C, as shown in Fig. 3(a). The EDX measurement results indicate that when the growth temperatures are at 750, 850, 900 and 1000 °C, the corresponding molar ratios of Mg in $Zn_{1-x}Mg_xO$ nanomaterials are determined to be $x = 2.87\%$, 3.51%, 4.43% and 5.01%, respectively. The Mg content is increased with the increase of growth temperature. It is worth noting that all the samples were prepared under the same condition, the only difference is the growth temperature, so, the difference of Mg content in $Zn_{1-x}Mg_xO$ nanomaterials is induced by the growth temperature, because that the increasing amount of Mg atom was vaporized with the increase

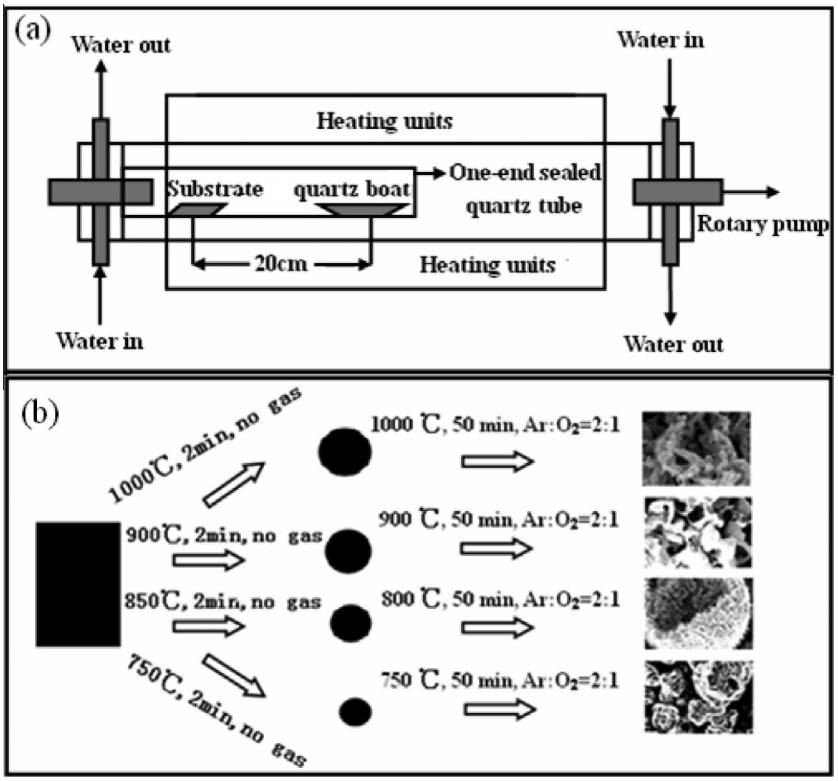

Fig. 1. (a) Schematic diagram of the experimental apparatus for the growth of $Zn_{1-x}Mg_xO$ nanomaterials. (b) Schematic illustration of the formation of $Zn_{1-x}Mg_xO$ nanomaterials.