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Synthesis, photoluminescence and ultrafast nonlinear optical properties of copper nanolayers/particles uniformly decorated ZnO nanowires

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ABSTRACT

Copper (Cu) nanolayers/particles decorated zinc oxide (Cu-ZnO) nanowires have been successfully synthesized by two-step chemical vapour deposition to prepare ZnO nanowires and magnetron sputtering method to deposit Cu nanolayers/particles. The field emission scanning electron microscopy images indicated the Cu nanolayers/particles are clearly visualized on surface of ZnO nanowires. The impact of sputtering time and sputtering power was analyzed. The results show that the atomic percent of Cu was gradually increased with the sputtering time and sputtering power was increased. The photoluminescence results demonstrated two major emission peaks for the Cu-ZnO nanowires, and the visible emission peaks of Cu-ZnO nanowires stronger than that of unmodified ZnO nanowires. Moreover, the results of open-aperture Z-scan measurements that all samples show the two-photon absorption behavior, and the two-photon absorption coefficients of Cu-ZnO is higher than that of unmodified ZnO nanowires. The results of closed-aperture Z-scan results demonstrated that all samples show self-focusing optical nonlinearity. These studies promise their potential applications in multifunctional optical devices.

1. Introduction

Up to now, various semiconductor composites modified with metal/nonmetal have been reported [1–3]. However, metal/nonmetal (such as noble metal and graphene) doped or decorated semiconductor has been demonstrated with the improved optoelectronic, photoelectrochemical and optical properties, etc [4–6]. For example, Baitimirova et al. [4] studied the structural and optical properties of graphene/ZnO nanolaminates. Rauwel et al. [5] studied the synthesis and photoluminescence properties of Hybrid ZnO and carbon nanomaterials. Viter et al. [6] reported the influence of localized plasmons on the optical properties of Au/ZnO nanostructures. Among, the advantages of metal and ZnO compound materials, which makes them promising material for technological applications in photocatalytic activities, piezoelectric transducers, phosphors, sensors, UV Photodetectors and UV lasers [7–9]. Moreover, Amongst various metal the surface plasmon resonance (SPR) effect of noble metal can expand the response range of incident light, increase optical absorption enrich light electrons in the electrode of light transmission rate, prolong the life of electronic, and inhibit photoproduction electronic-hole composite [10], etc. In a previous report, Au and Ag decorated oxide photoanodes were prepared [11,12], for which the absorption of visible light was enhanced and the combination of photogenerated electron-holes was suppressed. Su et al. [13] studied the surface-plasmon-resonance and band bending effects on the photoluminescence enhancement of Ag-decorated ZnO nanorods. Zhang et al. [14] studied enhanced ultraviolet emission from Au/Ag-nanoparticles @MgO/ZnO heterostructure light-emitting diodes: A combined effect of exciton- and photon- localized surface plasmon couplings. Our group has also done some works on Ag decorated ZnO nanowires [15]. The effect of Ag on the structural and optical properties of nanowires is reported. We report the PL properties of silver nanoparticles uniformly decorated ZnO nanowires. The mechanism of PL for A-ZnO nanowires was analyzed. However, syntheses, structural and physical properties Cu decorated ZnO have not been reported.

In present paper, Cu nanolayers/particles-decorated ZnO (Cu-ZnO) nanowires composite successfully synthesized by two-step chemical vapour deposition (CVD) and magnetron sputtering (MS) method. The obtained morphology and structure of Cu-ZnO nanowires were studied by using field emission scanning electron microscopy (FE-SEM, Quanta 200F) and X-ray diffraction (XRD, D/max-2600/PC) techniques. We study the effect of sputtering time and sputtering power on the morphologies and optical properties of Cu-ZnO nanowires. The results indicated that the atomic percent

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of Cu was gradually increased with the sputtering time and sputtering power was increased. The PL obtain results demonstrated two major emission peaks for the Cu-ZnO nanowires, and the visible emission peaks of Cu-ZnO nanowires stronger than that of unmodified ZnO nanowires. The ultrafast nonlinear optical properties of Cu-ZnO nanowires were studied by femtosecond Z-scan technique. Due to its good structure and performance, the samples were expected to have the potential applications in photoelectric devices.

2. Experiment

The Cu-ZnO nanowires were grown on quartz substrates by two-step process including CVD and MS method. The process schematic is depicted in Scheme 1. The quartz substrate was ultrasonically cleaned in acetone, rinsed in deionized water and subsequently dried in a flowing nitrogen gas before deposition. Then, the ZnO nanowires were grown by the CVD. Deposition of Cu (Cu target: 99.99% purity, 60 mm diameter, 4 mm thickness) nanolayers/particles on a quartz substrate with zinc oxide nanowires by using a MS method. The Cu nanolayers/particles were deposited on quartz substrates with ZnO nanowires by using MS system. The precursor is the ZnO (1 g, 99.99%) powder, which was placed into an alumina boat and loaded into the tubular furnace. The Au-coated quartz substrates were placed downstream from the powders. The furnace was heated to a preset temperature of 1250 °C. Ar was used as carrier gas during growth at the constant flow rate of 100 sccm and pressure of 50 Pa. Then, the furnace was naturally cooled down to room temperature. During the deposition process, the base pressure in the deposition chamber and radio frequency power were 6.0×10^{-4} Pa and 5 W (for sputtering time of 80 s, 100 s and 120 s), 10 W (for sputtering time of 100 s) and 20 W (for sputtering time of 100 s), respectively. The sample deposition was performed in the growth ambient with the sputtering Ar of 20 sccm at a constant working pressure of 2.0 Pa.

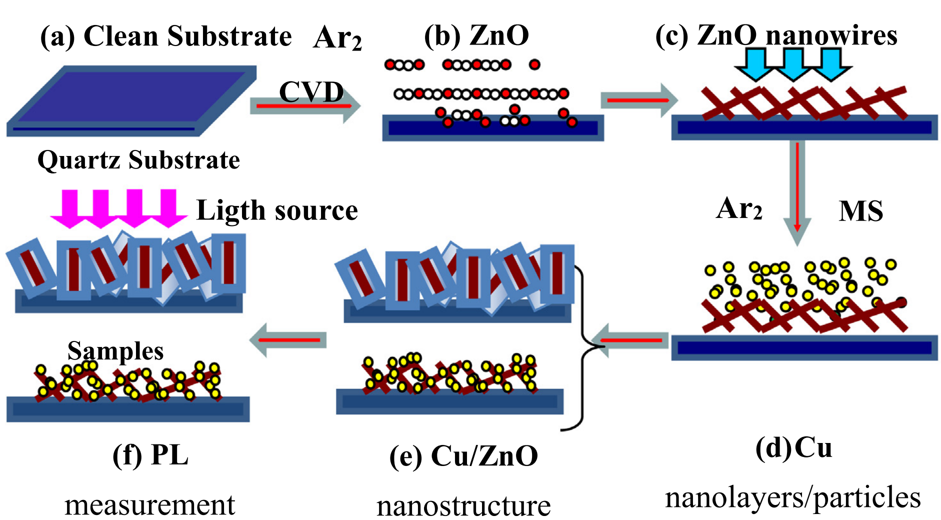
The structural properties of Cu-ZnO and ZnO nanowires were studied by FE-SEM. The crystallinity was analyzed by XRD equipped with monochromated Cu Ka irradiation. A room temperature PL spectra measurement was employed to study the optical properties. The excitation laser was a He–Cd laser with a wavelength of 325 nm, and the spectra range of 350–800 nm. The Z-scan experiments [16] are performed using a Q-switched, frequency doubled Ti:sapphire laser producing 100 fs laser pulses with a pulse repetition rate of 1 KHz at wavelength of 400 nm. Basically, in this technique the nonlinear sample is scanned through the focal plane of a tightly focused Gaussian beam. Unstability of the Gaussian beam intensity is ±0.2%. The pulse energies at the output of the laser system were 40.2 μJ with linear polarization.

3. Results and discussion

Fig. 1 (M_1, M = a, b, c, e, f) shows the top-view FE-SEM images of the unmodified ZnO and Cu-ZnO nanowires grown on the quartz substrates. Fig. 1 (M2) is magnified SEM images of such structures. As the evaporation time was increased, the atomic percent of Cu was gradually increased. According to the inset of Fig. 2 (M1) it can be observed size distribution diagram ZnO nanowires and Cu nanolayers/particles for each sample. The average diameter of ZnO nanowires was several decade nanometers. The average diameter of Cu nanolayers was several nanometers. The average diameter of Cu nanoparticles was more than twenty nanometers. A typical energy dispersive X-ray (EDX, Quanta 200F) spectrum of the Cu-ZnO nanowires is plotted in Fig. 1 (M_3). For Cu-ZnO nanowires, the clear peaks of oxygen, Zn, and Cu were observed in EDX spectra.

The XRD was carried out to investigate the structure of Cu-ZnO nanowires. As shown in Fig. 2 (M), all of patterns revealed a strong characteristic peak for the (0 0 2) plane reflections from hexagonal wurtzite structure ZnO. The other diffraction peaks are caused by the presence of Cu and Zn in the synthesized film. The peaks at two theta can be assigned to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), and (1 1 0) planes of ZnO. Moreover, the peak at 2θ values of ~44.2°corresponding to lattice planes of standard crystalline Cu metal, (good agreement with the CCID file no. 040836 cubic). The position of the peak is very consistent with the literature values [17].

Fig. 3(a) and (b) show the relationship between atomic percent of Cu and sputtering time/power, respectively. The results show that the Cu at. % increased with the increase of sputtering time/power. The morphologies and nanostructures of the Cu-ZnO nanowires with Cu nanolayers/particles were characterized by the transmission electron microscopy (TEM, H-7650). The results demonstrate that Cu nanolayers/particles were uniformly



Scheme 1. A schematic illustration of the fabrication processes of Cu-ZnO nanowires: (a) Quartz Substrate Cleaned using the modified dip-coating method; (b) the ZnO nanowires etched by Ar carrier gas; (c) ZnO nanowires the as-deposited; (d) Cu nanolayers/particles produced by sputtering for different time; (e) Cu/ZnO nanostructure; (f) PL measurement.

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