Low temperature synthesis and characterization of large scale ZnMgO nanowires

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ABSTRACT

Large scale ZnMgO nanowire array and network with tunable shapes has been successfully synthesized on solid Si substrate and flexible Au coated plastic substrate using low temperature hydrothermal synthesis technique. The diameters of the nanowires have been controlled in the range of 30-600 nm. Field-emission scanning electron microscopy (FESEM) was used to investigate the surface morphologies and orientations of the nanowires. The energy dispersive X-ray spectroscopy (EDS) indicates that the Mg concentration in the ZnMgO nanowires can reach ~2-5 atomic percent. To confirm the alloying process of Mg into ZnO and its distribution during the growth process, Auger electron spectroscopy (AES) was carried out for quantitative analysis of the surface composition profile of typical ZnMgO nanowires.

Keywords: Nanowires, Semiconductor, Synthesis, ZnMgO

1 INTRODUCTION

One dimensional (1D) nanostructures, as a unique low-dimensional nanoscale system, have carried a broad spectrum of extensive research due to their superior properties such as high surface to volume ratio, high crystallinity and quantum confinement effect. For instance, semiconductor oxides such as ZnO have superior chemical and thermal stability as well as specific electrical and optoelectronic properties with a broad range of potential applications[1]. ZnMgO is regarded as an ideal material for ZnO based optoelectronic devices. By alloying with MgO, which has a cubic structure and a broader direct band gap of 7.7 eV, the band gap of ZnO can be remarkably blue-shifted for the realization of light-emitting devices operating in a wider wavelength region[2]. In addition, alloying ZnO with Mg makes ZnMgO a potential candidate for future optoelectronic devices because of its wide band-gap, less lattice mismatch with ZnO as the ionic radius of Mg^{2+} and Zn^{2+} are similar[3,4]. ZnMgO 1D nanostructures[5,6], such as nanowires, nanorods, nanopillars and ZnO/$Zn_{1-x}Mg_xO$ nanoheterostructures[7-10] along an axial or radial direction have been mostly fabricated using vapor phased deposition techniques such as metalorganic vapor phase epitaxy (MOVPE)[5], pulsed laser deposition (PLD)[6], molecular beam epitaxy (MBE)[12], RF magnetron co-sputtering[13], thermal evaporation[14] and vapor transport[15] to obtain high-performance nanometer scale optoelectronic devices. In contrast to vapor phase techniques, there have been significantly fewer reports of ZnMgO NWs grown by wet chemical synthesis approaches due to a significant difficulty to alloy Mg into ZnO lattice at usually much lower processing temperature. However, it is worth noting that wet chemical methods such as hydrothermal synthesis process have several advantages over the other growth processes including catalyst-free growth, low cost, large yield, environmental friendliness and low reaction temperature. Here, we report the synthesis and characterization of large scale ZnMgO NWs on solid Si and flexible polymer substrates by hydrothermal method.

2 EXPERIMENTAL PROCEDURES

Three types of substrates have been used: Si (100) substrates, ZnO nanoparticle-seeded Si (100) substrates and Au-coated flexible plastic substrates. Before Au coating and ZnO seeding, the silicon and plastic substrates were cleaned by deionized water and ethanol 2-3 times and then passed through the plasma cleaning for 40 minutes. For the plastic substrates, a ~20 nm thick Au coating was deposited using a POLARON DC sputtering unit. On the second type of Si substrates, ZnO nanoparticle seeds were made using a sol-gel method. The ZnMgO NWs growth on Si and Au-coated plastic substrates were conducted by keeping the substrates in an autoclave filled with an aqueous solution of $Zn(NO_3)_2.6H_2O$, Hexamethylenetetramine (HMT) and $Mg(NO_3)_2.6H_2O$ in an 1:1:2 ratio at 165 °C for 6 hours. The PH value of the solution before reaction was kept as 7 and after reaction as 9. For the ZnMgO growth on ZnO seeded substrates, a two-step process was used. Firstly, Si substrates were put into solution of $Zn(NO_3)_2.6H_2O$ and HMT in 1:1 ratio at 80 °C for 4 hours, in order to grow a uniform layer of ZnO nanowires on the substrates. Second, the grown ZnO NWs-on Si substrate after the first step was immersed into the solution of $Zn(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$ and HMT in an 1:2:1 ratio at 155 °C with PH value 7 in an autoclave for 4 hours. For all the samples, substrates were removed from the solution, rinsed with deionized water and dried in air at 80 °C overnight. The morphology and the orientation of the nanowires were

investigated by a JEOL 6335F field emission scanning electron microscope (FESEM) and a BRUKER AXS D5005 (Cu *Kα* radiation, λ=1.540598 Å) X-ray diffractometer (XRD). The chemical composition of ZnMgO NWs on the Si substrates was examined using energy dispersive X-ray spectroscopy (EDXS) in the FESEM and a Phi 595 Scanning Auger spectrometer (AES).

3 RESULTS AND DISCUSSION

3.1 Si substates

Figure 1(a) shows a typical XRD spectrum of the as prepared samples on Si substrates. Three major peaks were resolved to be closely matched to (100), (002) and (101) atomic planes in wurtzite structured ZnO, revealing their good crystallinity. The peak (002) nearly matched to ZnO because of a rather low-concentration of Mg in the NWs, as indicated in the EDS data in figure 2. Figures 1(b) and 1(c) are respectively a low-magnification and high-magnification SEM images showing the grown free-standing ZnMgO micro- and NWs, with a diameter range of ~1 micrometer to ~200-250 nm. The careful observation of the bigger NWs reveals that each individual micro-wire is composed of smaller NWs as the red arrowheads indicated in figure 1(c).

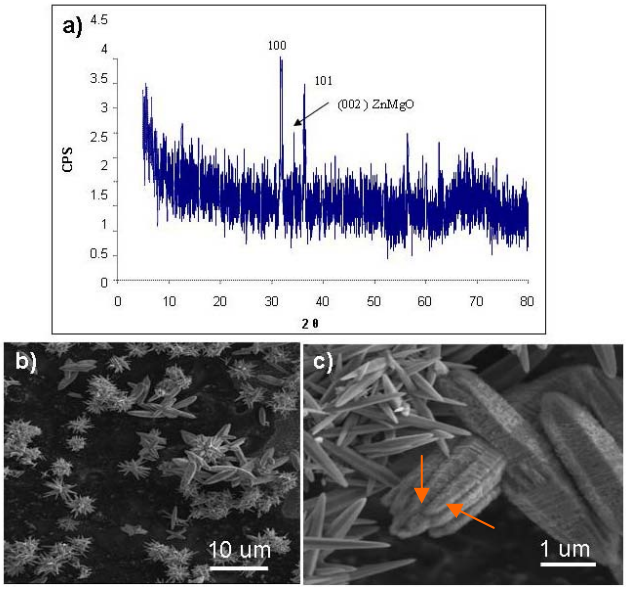

Figure 1: (a) A typical XRD spectrum of free-standing ZnMgO NWs samples. (b) a low-magnification and (c)high-magnification SEM images showing the grown free-standing ZnMgO micro-wires and NWs.

The EDS spectra shown in figure 2(a) and 2(b) are respectively collected from the area with bigger micro wires and smaller nanowires. They both reveal that only C, O, Zn, Si and Mg were present. Both spectra confirmed the presence of Mg in individual micro- and nanowires although the atomic percentage of the Mg is quite low in both cases. In the micro-wires the at. % of Mg was 1.72, which clearly indicates the presence of Mg in NWs. While in the smaller NWs, only 0.41 at. % of Mg was present. The carbon and Si peaks are respectively contributed by a possible contamination during sample preparation and the substrates.

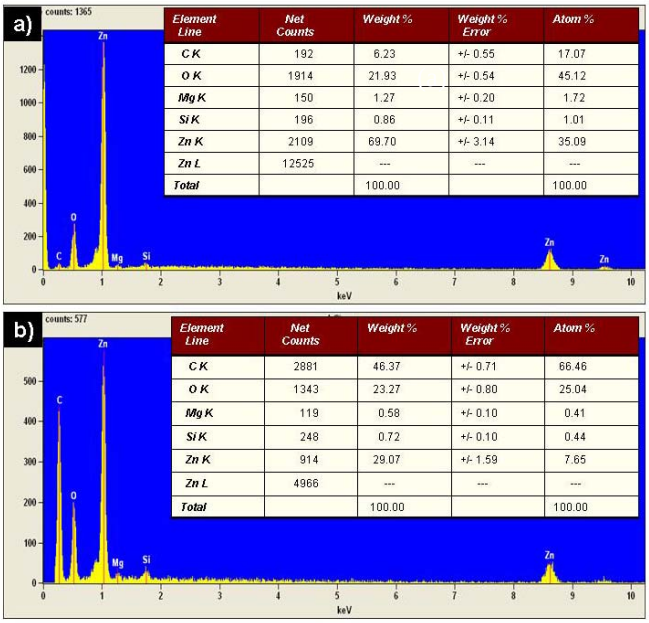

Figure 2: (a) An EDS spectrum of the bigger ZnMgO micro-wires. (b) An EDS spectrum of the smaller ZnMgO nanowires.

3.2 ZnO nanoparticle-seeded Si substrates

Figure 3(a) shows a typical SEM image of the vertically aligned ZnO NWs on the ZnO nanoparticle-seeded Si (100) substrates. The ZnO NWs have a uniform diameter of ~30-40 nm and a length of ~1 μm. The NWs are densely packed and uniform all over the whole silicon substrate. Figure 3(b) shows a typical low-magnification SEM image of the grown NWs after the second step reaction. It is found that the array pattern kept the same, and the length of the NWs remained the same but top portion of each NW changed into cone shape.

The inset in Figure 3(b) reveals the EDXS analysis result from the grown ZnMgO NWs samples corresponding to the dotted square area in the NW arrays. From the shown spectrum, the Mg content was revealed to be ~3.45 at. % (± 0.55 at. % errors). Different area EDXS analysis results have shown that a ~2-5 at. % Mg was generally achieved in the ZnMgO NW arrays after the 2-step hydrothermal processing.

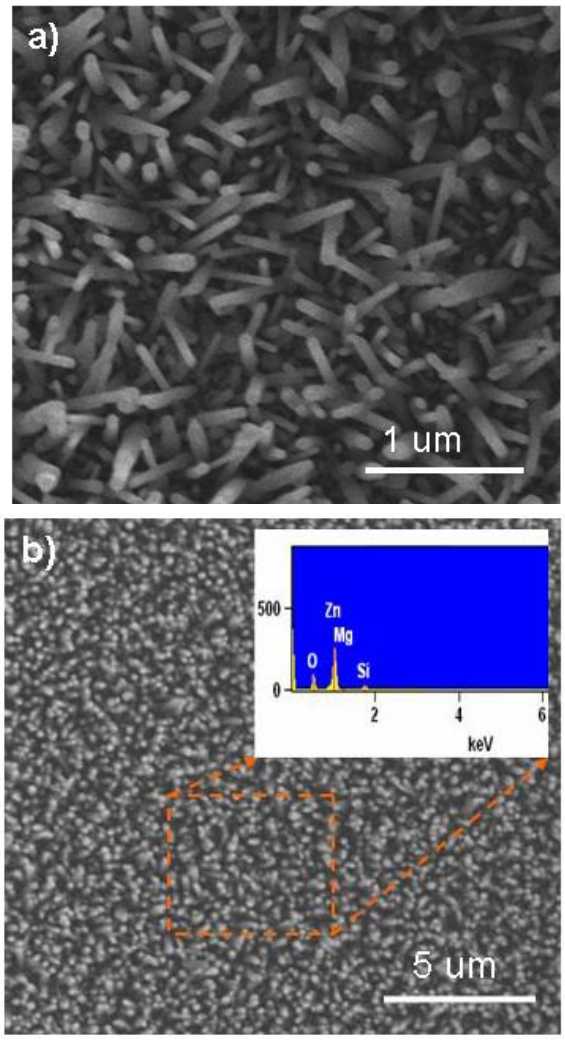

Figure 3: (a) ZnO NW arrays grown on ZnO seed. (b) ZnMgO NW arrays after the second step reaction, inset shows a typical EDS spectrum from dotted square area of NW arrays.

To further confirm the Mg content in the grown NWs, Phi 595 Scanning Auger spectrometer was used for the AES spectra. AES spectra survey obtained from the 2-step grown ZnMgO NW arrays and its chemical composition was determined. Figures 4(a) and 4(b) are AES spectra of the ZMO NWs respectively scanned in a full scan range (40-1100 eV) and the closer view in the Mg peak area. After differential calculus analysis some obvious peaks indicated the presence of Mg, Si, C, O and Zn. The Mg has a ~16.3% atomic concentration, much higher than the one detected in EDS results, which suggested that the Mg alloying in the hydrothermal synthesis here might not be uniform. Further improvement on the processing parameters will be done in the near future.

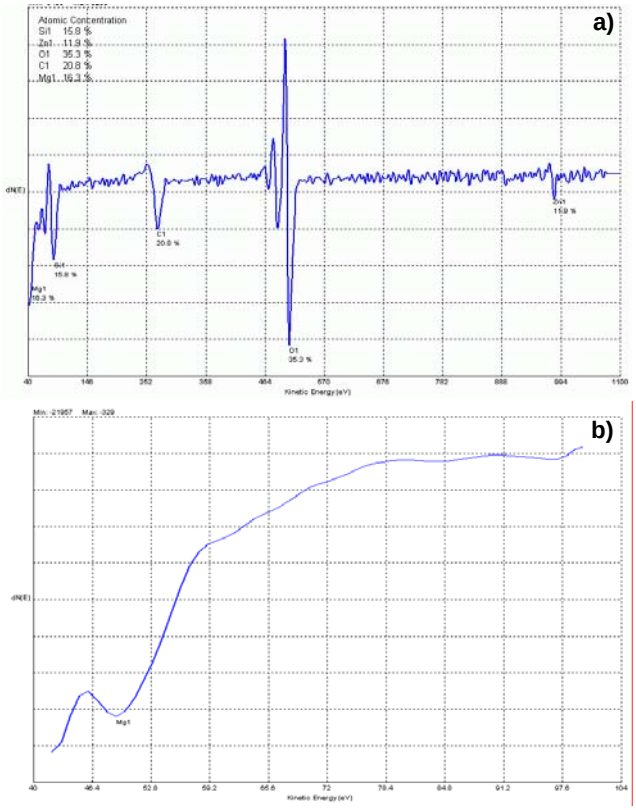

Figure 4: (a) a full scale scanning result of AES spectra. (b) a AES spectrum showing the presence of Mg.

3.3 Au-coated flexible substrates

Figure 5 shows the ZnMgO NWs grown on Au-coated flexible plastic substrates. Sparsely grown ZnMgO NWs have been fabricated normal to the substrates, with a diameter range of 200-600 nm. From the Figures 5(a) and 5(b), most of the aligned NW tips have been interconnected by nanofibres with a diameter range of ~50-100 nm Figure 5(c) shows the clear cone shape of ZMO NW, with top diameter of around 150 to 200 nm and the bottom diameter of around 450 to 500 nm. Figure 5(c) displays the hexagonal structure of the NWs. The EDXS analysis indicated that 1.20 at. % of Mg presented corresponding to the top-square portion of the NWs. The EDXS spectrum also revealed the presence of an excessive carbon amount in this sample, which might suggested that the interconnecting nanofibres might be of carbon-based polymer so as to contribute to the carbon composition.

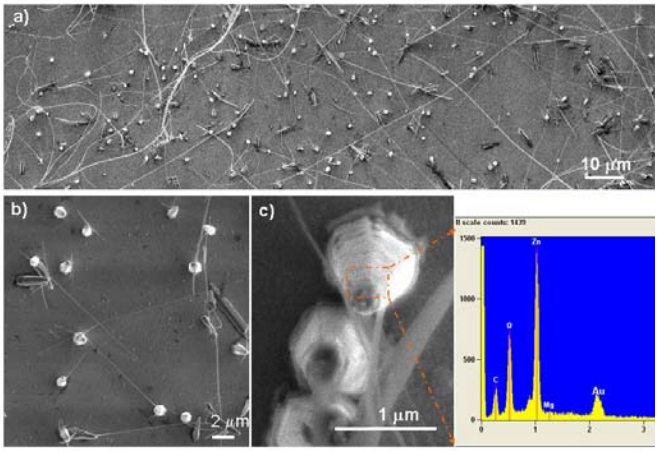

Figure 5: Typical SEM images of (a) ZnMgO NWs interconnected by possibly polymer nanofibres on Au-coated plastic substrates. (b) vertically aligned ZnMgO NWs. (c) closer view of ~1 µm long and cone-shaped ZnMgO NWs with corresponding EDS spectrum for a tip portion.

4 CONCLUSIONS

. In summary, large scale ZnMgO nanowire array and network has been successfully synthesized on solid Si substrate and flexible Au coated plastic substrate using low temperature hydrothermal synthesis technique. The diameters of the nanowires have been controlled in the range of 30-600 nm. Field-emission scanning electron microscopy (FESEM) was used to investigate the surface morphologies and orientations of the nanowires. The energy dispersive X-ray spectroscopy (EDS) indicates that the Mg concentration in the ZnMgO nanowires can reach ~2-5 atomic percent. To confirm the alloying process of Mg into ZnO and its distribution during the growth process, Auger electron spectroscopy (AES) was also carried out for quantitative analysis of the surface composition profile of typical ZnMgO nanowires.

Further detailed transmission electron microscopy (TEM) and SEM structure, morphology and chemical analysis, as well as kinetics and optics studies of the ZnMgO NW array and the interconnected ZnMgO NWs are on-going, which will be discussed elsewhere [16].

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