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Identification and characteristics of ZnO/MgO core-shell nanowires

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In this paper, ZnO/MgO core-shell nanowires are synthesized based on a one-step chemical vapor deposition (CVD) method. The scanning electron microscopy (SEM) images of core-shell nanowires indicate that Mg addition has little influence on the morphology of the synthesizing products. High crystalline quality ZnO/MgO core-shell nanowires instead of ZnMgO ternary compounds are identified by X-ray diffraction (XRD) patterns, transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) pattern and photoluminescence (PL) spectra. The experimental results show that the ultraviolet (UV) emission of these samples with MgO shell is 12 times higher than that of the corresponding bare ZnO nanowires, and the suppression of the green emission is only 1/45 of the bare ZnO nanowires. It is also found that PL properties are proportional to Mg ratio. The UV emission enhancement and green emission suppression are due to the passivation of surface defects and the improvement of ZnO crystalline quality. The results are very useful for the development of optical devices based on nanowires. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

I. INTRODUCTION

ZnO has widely been used as the material for transparent electrode, photodetector, laser and photodiode. Compared to ZnO film and bulk material, ZnO nanowires have better performance in the photoelectric conversion and the transmission for the quantum confinement effect. Although papers have been published regarding the preparation and applications of ZnO nanowire, P-type doping and band-gap engineering are still two main obstacles for the commercial applications. Large surface-to-volume ratio induces high density defects on the surface of ZnO nanowires. By depositing a layer of shell on nanowires to fabricate core/shell nanostructure, the surface states of the core are modified, and the bandgap of the core material can be tailored. As a result, the properties including photoluminescence (PL) performance of the core are improved. ZnO/MgO core-shell nanowires can be post-annealed to produce ZnMgO structure, and the core-shell structure has higher photoluminescence performance over bare ZnO nanowires. Due to MgO coating, the improved performance can significantly passivate the surface defects of ZnO nanowires. Nanoscale heterojunction has higher carrier injection efficiency compared with ZnO/MgO film structure. Yang et al. has reported electrically pumped near-ultraviolet lasing from ZnO/MgO core shell structure. Y. Wu discussed highly crystalline quality core-shell ZnO/MgO nanowires with great UV emission improvement. There several methods have been developed to synthesize ZnO/MgO core-shell nanostructures. Most of these methods are carried out by a two-step process in which the preparation of ZnO core and MgO shell are conducted separately. Hydrothermal growth methods are the common way of preparing MgO shell. However, two-step process is difficult to obtain consistent experimental results. MgO shell synthesized by hydrothermal growth...
methods are usually polycrystalline structure and in poor morphology. Therefore, it is difficult to synthesize ZnO/MgO core-shell nanowires with good morphology and high crystal quality.

In this paper, we proposed a one-step method for the fabrication of ZnO/MgO core-shell nanowires with good morphology and advanced photoluminescence performance by one-step chemical vapor deposition (CVD) method.

II. EXPERIMENTS

The growth of ZnO/MgO core-shell nanowires was performed in a horizontal vacuum furnace. Tube-in-tube configuration including a quartz tube vacuum chamber and a smaller quartz tube were used in the experiments. High purity ZnO powder (99.99%) and commercial graphite powders were used as Zn source. Pure Mg powder (99.9%) was used as Mg source. ZnO and graphite powders were fully mixed with equal weight of 0.5 g and were placed in an Al₂O₃ boat. Silicon wafer sputtered with 5nm Au buffer layer was cut into 1 cm × 1 cm square pieces that were positioned in another Al₂O₃ boat. 0/0.02/0.03/0.06 g Mg powder was positioned in the same boat with Si substrate. The Mg atomic ratios of original reactants in four groups of experiments were 0%, 12%, 17% and 29% respectively. The second Al₂O₃ boat was also inserted into the small one-ended quartz tube next to the first boat loading with ZnO and carbon powders. Small quartz tube was inserted into quartz tube vacuum chamber. Both Al₂O₃ boats were heated up to 950°C with heating speed of 40°C/min. The quartz tube vacuum chamber was filled with pure Ar atmosphere and maintained pressure at 1 atm during the heating process. The configuration schematic diagram used for synthesizing ZnO/MgO nanowires was shown in Figure 1. When the temperature reached up to 950°C, the vacuum chamber pressure was dropped down to 10 Torr in less than one minute. And then 100sccm Ar/O₂ mixture flow (Mol Ar : Mol O₂ = 9 : 1) was imported. The pump kept working during the whole process to guarantee constant chamber pressure of 10 Torr. This synthesizing process was kept for 40 minutes. Finally, the chamber pressure returned to 1 atm by importing pure Ar and the temperature gradually returned to room temperature by natural cooling.

The morphology of nanowires was investigated by field emission scanning electron microscopy (FESEM, SU-8010) and transmission electron microscope (TEM, JEM-200CF). The X-ray diffraction (XRD) patterns were obtained using a XRD-7000 diffractometer. The elemental contents were investigated using energy dispersive X-ray analysis (EDAX, TEAM Apollo XL EDS). The optical properties of the ZnO/MgO core-shell nanowires were studied using photoluminescence spectroscopy (Steady-State & Time-Resolved Fluorescence Spectrofluorometer QM4) and a He-Cd laser with excitation wavelength of 325 nm was employed.

III. RESULTS AND DISCUSSION

SEM images and EDAX patterns were shown in Figure 2. There were four groups of contrast experiments with different original Mg dosage in reactants.

![FIG. 1. Schematic diagram of configuration used for synthesizing ZnO/MgO nanowires.](image-url)
FIG. 2. Typical low magnification SEM images of ZnO/MgO nanowires (a) (c) (e) (g) and EDAX patterns of ZnO/MgO nanowires (b) (d) (f) (h) with different Mg atomic ratio of 0%, 12%, 17%, and 29% in reactants respectively.

The EDAX spectrum can only be used to qualitatively estimate element proportion, so the original Mg atomic ratio \((M_{\text{Mg}}/(M_{\text{Mg}} + M_{\text{ZnO}}))\) of 0%, 12%, 17% and 29% in reactants were used in the following discussion. These numbers can only reveal that Mg concentration gradually increased with the proportion of the Mg dosage but not indicated the exact Mg percentage in nanowires.
According to the results shown in the SEM images, almost the same morphology was achieved in these nanowires with different original Mg atomic ratio. The synthesizing nanowires had great uniformity in length (about 10 ~ 15 µm) and diameter (about 100 ~ 200 nm). When the nanowires were thinner, and the aspect ratio was larger, there were correspondingly more surface defects. The directions of nanowires growth were tanglesome because of polycrystalline silicon substrate. Figures 2(b), 2(d), 2(f) and 2(h) display EDAX spectrum of these samples for the purpose of element analysis. Mg element was not visible in EDAX spectrum until Mg atomic ratio in reactant was large enough, about 12% ~ 17%. When Mg dosage increased, the Mg peak in EDAX spectrum was more obvious. It can be clearly seen that Mg proportion of nanowires was quite sensitive to Mg dosage in Figures 2(f) and 2(h). Additionally, Mg content in nanowires had no influence on the morphology of products. It was different from the two step synthesizing process. In the two step synthesizing process, the morphology of the bare ZnO nanowires was quite different from that of the core-shell nanowires. In Figure 3(a), there were no nanowires grow on the bare Si substrate without Au catalyst, so VLS (Vapor-Liquid-Solid) mechanism worked at the initial nanowires nucleation stage. Since there were no Au catalyst particle at the tip of ZnO nanowire in Figure 3(b), VS (Vapor-Solid) mechanism was reasonable to explain the nanowires growing process.

We can see from the EDX spectrum that there were both Mg and Zn element. XRD patterns were used to analyze crystal structure and structure variation of the grown products. The XRD pattern of grown products with different Mg atomic ratio in reactant was shown in Figure 4. It indicated good crystal purity without any impurities. Pure ZnO with major peaks of (100), (002) and
(101) planes correspond to a wurtzite ZnO crystal structure (JCDPS 05-0664). With the addition of Mg powder, some weak lines were found to coincide with the cubic MgO (JCPDS 04-0849) of (200) and (220) peaks. With the increase of Mg ratio from 12%, 17% to 29%, peaks intensity of (200) and (220) increased correspondingly. There was no Mg element in nanowires for 12% Mg atomic ratio indicating in EDAX spectrum, but there was a weak MgO (200) peak shown in XRD patterns. Because the ionic radius of the Mg$^{2+}$ ($r_{\text{Mg}}^{2+} = 0.057 \text{ nm}$) was smaller than that of Zn$^{2+}$ ($r_{\text{Zn}}^{2+} = 0.06 \text{ nm}$), Mg doping caused a slight shift of the (002) XRD peaks toward higher diffraction angles and the shift depended on the Mg content in the nanowires. However, there was no ZnO (002) peak shift in Figure 4. It was an indirect evidence for ZnO/MgO core-shell nanowires.

The TEM images for Mg atomic ratio of 17% were shown in Figure 5. The smooth nanowires surface indicated that there was little lattice imperfection. The apparent protuberance was reported in other papers as well. From Figure 5(b) we can identify core-shell boundary obviously from TEM image. This was direct evidence of core-shell structure. The magnified HRTEM image obtained from the core-shell interface in the lower region of a nanowire was shown in Figure 5(d). The planar distance of the dotted lines indicated in these phases was 0.21nm and the crystal structure of these phases was not wurtzite but cubic. Thus, the lattice constant and the crystal structure of this region were identical to those of bulk MgO. The selected area electron diffraction (SAED) pattern of the surface for this nanowire was shown in Figure 5(c). Standard cubic rocksalt crystal structure shown in SAED pattern corresponds to the high quality singlecrystal MgO for the outer layer region.
FIG. 6. (a) Full-scale semi-logarithmic plots of room temperature PL spectra of nanowires with Mg atomic ratio of 0%, 12%, 17% and 29% in reactants (b) Relative UV emission intensity and Green emission intensity with the increase of Mg atomic ratio.

Based on these observations, it can be confirmed that the nanowires were ZnO/MgO core-shell nanowires instead of ZnMgO ternary compounds.

The room-temperature PL spectra of bare ZnO nanowires and nanowires with different Mg dosage shown in Figure 6(a) were measured using a He-Cd laser as exciton source with the wavelength of 325 nm. All the products displayed two typical emission peak, near-band-edge (NBE) UV emission and defect green emission, corresponding to ZnO. PL spectra were powerful for investigating both core-shell ZnO/MgO nanostructure and Mg doping ZnO nanostructures, because both showed different PL performance compared to pure ZnO nanostructures. For Mg doping ZnMgO nanowires, the blue shift of UV emission was expected as a result of the Burstein-Moss effect due to Mg$^{2+}$ substitution of Zn$^{2+}$. The blue-shift of the UV peak increased with the increase of Mg concentration. As shown in Figure 6(a), the near-band-edge UV emission peak at ~388 nm, so there was no shift compared with pure ZnO nanowires. And there was no Mg element diffusing into ZnO core and no ZnMgO ternary compounds formed in these nanowires. According to the Burstein-Moss effect, Mg doping can effectively adjusts band-gap of ZnO nanowires and results in blue-shift of NBE peak.
For core-shell structure nanowires, the formation of ZnO/MgO interface layer with highly crystalline quality can effectively passivate surface defects of ZnO nanowires. Correspondingly, the green emission intensity arising from the surface defects was greatly suppressed and the UV emission intensity was improved as a result of better ZnO crystal quality. The PL spectra of the bare ZnO nanowires shown in Figure 6(a) included a strong broad green emission peak at ~520 nm and weak near-hand-edge UV emission peak at ~388 nm. The origin of the UV emission peak was attributed to the free exciton emission of ZnO. As a result of discontinued lattice atomic arrangement on surface, there were much more hanging bonds and oxygen vacancy (V\text{O}) on the surfaces of bare ZnO nanowires compared to the inner region. Generally, when the diameter of nanowires was thinner, V\text{O} was larger. Correspondingly, the green emission was stronger, and the UV emission was weaker. Like the SEM image shown in Figure 2(a), the length of nanowire was 15 µm but the diameter was only about 150 nm. It indicated ultrahigh surface-to-volume ratio and this was in good correspondence with the PL spectra shown in Figure 6(a). With the increase of Mg atomic ratio in reactants from zero to 12%, 17% and 29%, the UV emission intensity was significantly improved and that the green emission intensity was evidently suppressed. For the nanowires with original Mg atomic ratio 12%, 17% and 29%, the UV emission intensity was about 4, 7 and 12 times higher than the bare ZnO nanowires. For the nanowires with 29% Mg atomic ratio, its green emission intensity was weaker. Relative green emission intensity was showed in the same horizontal axis. NBE UV emission increased rapidly while the defect green emission showed a sharp drop with the increase of Mg dosage. The green emission was even negligible when Mg atomic ratio was more than 17%. This improvement was due to the formation of ZnO/MgO interface layer with highly crystalline quality. The ZnO/MgO core-shell structure was helpful in passivating the remained surface defects, providing confining barriers to electrons and holes within the ZnO core, and favoring excitonic ultraviolet radiative recombination, while suppressing defect-related luminescence in the visible and improving electrical conductivity. The PL performance improvement had potential applications in manufacturing high performance photoelectronic devices.

The original UV emission peak without blue-shift was attributed to the free exciton emission of the residual inner core of the nondiffused ZnO nanowires. The (002) ZnO XRD peaks in Figure 3 did not shift toward higher diffraction angles with the increase of Mg percentage, which was unmatched with Mg doping ZnO nanowires. Instead, a wurtzite ZnO crystal structure and cubic rocksalt crystal MgO structure can be identified in XRD patterns for nanowires with Mg addition. The HRTEM image and SAED pattern shown in Figure 5 were strong evidences for singlecrystal ZnO/MgO core-shell nanowires and MgO layer. The PL performance showed exact correspondence with ZnO/MgO core-shell nanowires instead of ZnMgO ternary nanowires. So the synthesizing products were ZnO/MgO core-shell nanowires with high crystal MgO layer, which effectively passivated surface defects of ZnO nanowires surfaces and produced excellent PL performance.

For this case, it was more appropriate to explain the growth of Au-catalyzed nanowires by a combination of VLS–VS mechanism instead of the conventional VLS mechanism. The CVD arrangement, one end was semi-enclosed and the other end was open, was different from the conventional installation. The semi-enclosed end permit proper oxygen volume that the reaction need flowing into the tube, since the oxygen volume was critical to the synthesizing of ZnO/MgO core-shell nanowires. According to Fick’s law, the diffusion always propagated toward the region with a lower concentration, so a little Mg vapor reached the Si substrate. In fact, there were no well crystallized samples that can be obtained when Mg source was placed in front of Si substrate, because the degradation of the preferred orientation was caused by the formation of mixed phases. The unique sequence of ZnO-Si-Mg was an explanation for that ZnO core firstly crystallized. Ar/O\text{2} main flow and Zn source were nearer than Mg source, so Zn vapor reached the substrate firstly and formed the ZnO core. Mg diffusion branch flow reached the substrate subsequently for the crystallization of MgO shell nanostructure.

The schematic diagram of ZnO/MgO core-shell nanowires growth mechanism was shown in Figure 7. Au-Si eutectic liquid alloy forming through cocrystallization effect acted as nucleation center at the initial nanowires growth stage because there was no nanowires growing on the bare Si substrate without Au catalyst. Au alloy droplets with higher sticking coefficient surface were more
energetically favored sites for Zn and O atoms than Si substrate. Successive incorporation of Zn and O atoms in Au alloy droplet produced supersaturation state and then Zn and O atoms crystallized forming ZnO nuclei. Base-growth mode instead of tip-growth mode of Au-catalyzed zinc oxide nanowires occurred in the synthesis process. And in base-growth mode, Au stayed at the surface of Si substrate rather than at the tip of nanowire. There was no Au particle at the tip of nanowires, so VS mechanism instead of VLS mechanism worked in the process of nanowires growth. VS mechanism occurred at the gas-solid interface between the vapor reactants and the exposed surface of the growing nanowires. The one end closed structure of the small tube led to high Zn vapor concentration. Due to the high Zn vapor concentration and large electronegativity difference between Zn and Au, ZnO nucleation center was formed. Along preferred growth direction, ZnO shell began to epitaxially grow on the surface of these thin ZnO nanowires. MgO shell inhibited the lateral growth of ZnO nanowires. Therefore, the core-shell ZnO/MgO nanowires with good morphology and crystal quality can be obtained.

IV. CONCLUSION

ZnO/MgO core shell nanowires with good morphology and high crystal quality synthesized by a simple one-step CVD method have been discussed. The EDAX spectra, the TEM images, the SAED pattern, the XRD patterns and the PL spectra were applied to confirm the ZnO/MgO core shell structure. The core-shell nanostructure was formed by epitaxial growth of MgO coating layer on the surface of core ZnO nanowires. The single crystal MgO shell was the reason of significant NBE emission enhancement and defect emission suppression of ZnO/MgO core-shell nanowires compared with bare ZnO nanowires in the PL spectra.

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