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Relationship Between Photoluminescence Properties of ZnO/CuO Core/Shell Nanowires and The Thickness of CuO Shells

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Abstract: ZnO/CuO one-dimensional core/shell nanowires have been synthesized by sequential growth of core and shell, respectively. Phase and structural analyses reveal that the ZnO core has single crystalline phase whereas the CuO shell has polycrystalline phase covering on the surface of the core. The photoluminescence (PL) properties of ZnO nanowires change with the CuO shell thickness. The photoluminescence intensity increases when the shell is very thin, which is attributed to the surface modification by CuO shell. When the shell gets thicker, the intensity of the photoluminescence does not change any more because a type-Ⅰ band alignment is formed between the core and shell. The experimental result is discussed.

Key words: ZnO/CuO; core/shell nanowires; photoluminescence properties; type-Ⅰ band alignment
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ZnO/CuO 核壳结构纳米线光致发光性能与 CuO 壳层厚度的关系

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摘要：通过分别生长核层与壳层制备出了ZnO/CuO核壳结构的纳米线。形貌和结构分析表明，ZnO核为单晶纳米线而CuO则以多晶形式覆盖在核层表面上。光致发光(PL)研究表明，ZnO纳米线PL强度随CuO壳层厚度的变化而变化。当壳层比较薄时ZnO的PL强度增大，这主要是由于CuO壳层对ZnO核层的修饰减少了表面态，而当壳层厚度增加到一定程度时，ZnO的PL强度不再变化，这主要是由于在核壳结构中形成了type-Ⅰ型结构的原因。我们对这一现象做了详细的讨论。

关　键　词：ZnO/CuO; 核壳结构纳米线; 光致发光性质; type-Ⅰ型结构

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1 Introduction

One-dimensional (1D) nanostructured oxides have received ever-increasing attention recently due to their intriguing properties and unique applications in novel nano-devices[1-3]. One of the most predominant properties of the 1D oxide nanowires is as optoelectronic materials, because the 1D nanowires provide direct path for carriers transporting. ZnO, as a stable n-type semiconductor with a large band gap ($E_g = 3.3$ eV at 300 K), is always considered as potential candidate for optoelectronic materials[4-6] because of its low-cost, non-toxic, and high electron mobility. As another important oxide semiconductor, CuO, has also drawn considerable attention, for its intrinsic p-type conductivity with narrow band-gap (1.2 ~ 1.9 eV), large photoconductivity and strong absorption in the visible region[7-8]. It is promising to fabricate ZnO/CuO core/shell p-n heterojunction nanostructures for optoelectronic and clean solar energy applications, considering their respect and combined advantages. For example, ZnO/CuO core/shell structures can enlarge the optical absorption range and improve solar device efficiencies, as the wide and narrow band gap of ZnO and CuO can respectively absorb UV and visible solar energies. Indeed, great effects have been put to their solar energy applications[7,9-10], and Zhao X H *et al*[7] have obtained a 0.71% photo-to-hydrogen conversion efficiency from photoelectrochemical water with ZnO/CuO core/shell nanowires. However, the optical properties of the core/shell structures have been seldom studied. Though Wang R C *et al*[11] obtained enhanced UV emission in ZnO-CuO core/shell nanorods, Zhu Y W *et al*[12] have studied the PL properties of ZnO/CuO as a function of Zn content.

To our knowledge, the photoluminescence properties of the ZnO/CuO core/shell structures as a function of shell thickness have never been reported. In this paper, we have successfully synthesized ZnO nanowire arrays by a simple hydrothermal method. After that the CuO shells with different thickness have been fabricated by soft chemical treatment of the as-synthesized ZnO nanowires. The structural and optical properties of the core/shell nanowires are studied. It is indicated that the ZnO core shows a near band edge emission centered at 378 nm. After CuO shell modification, the emissions spectral change with the thickness of CuO shells: the PL intensity first increases when the shell is thin and does not change any more when it saturates the surface dangling bonds of ZnO core. The reasons for these changes are attributed to the passivation of the surface states at the initial growth stage of the shell and the eventual formation of a type Ⅰ band alignment between the core and shell when the shells become thick.

2 Experiments

The samples are obtained through a two-step method. High aspect ratio ZnO nanowires are first synthesized by a simple hydrothermal method. Typically, 0.05 mol/L of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.05 mol/L of $C_6H_{12}N_4$ were initially dissolved in 30 mL of water under vigorous stirring to form a homogeneous mixture, the solution is then transferred to an Teflon autoclave.

The solution was allowed to reach to 180 ℃ and kept at this temperature for 3 h. The as-synthesized sample is then cut into pieces for the following growth of CuO shell. The preparation of CuO shell is carried out in two steps. First, ZnO samples are immersed in $Cu(NO_3)_2 \cdot 3H_2O$ solution for 30, 60 and 120 min, respectively. Then, the samples are annealed under oxygen atmosphere at 800 ℃ for 1 h. The as-synthesized sample and the samples treated for 30, 60, and 120 min are labeled as sample A, B, C and D, respectively. The samples are then characterized by a series of techniques. X-ray diffraction (XRD) techniques are done using Cu Kα irradiation on an 800 W Philips 1830 powder diffractometer. Field-emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray (EDX) analysis are acquired on a Hitachi S-4800 microscope instrument by using an accelerating voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) observations are carried out on a JEM-2010 microscope instrument by using an accelerating voltage of 200 kV. Steady state PL spectra are recorded by using a Princeton sp2500 spectrometer that utilized a 325 nm He-Cd laser line of 30 mW. All the measurements are performed at room temperature under the same conditions, the reproducibility of the samples is confirmed by measuring several points for the same sample.

3 Results and Discussion

The X-ray diffraction (XRD) patterns of the products from sample A to D are shown in Fig. 1, which reveal that the diffraction peak of the as-grown products (sample A) can be indexed to the wurtzite structure of ZnO. The strong and intense (002) diffraction peak indicates the nanowires are *c* axial preferred orientation. The peak structure remains almost the same for the short CuO treatment time (sample B). With the increasing treatment time of CuO, a new peak corresponding to the plane of monoclinic CuO gradually appears in sample C to D, indicating that CuO has successfully covered on the core surface and its thickness increase with the increase of treatment time.

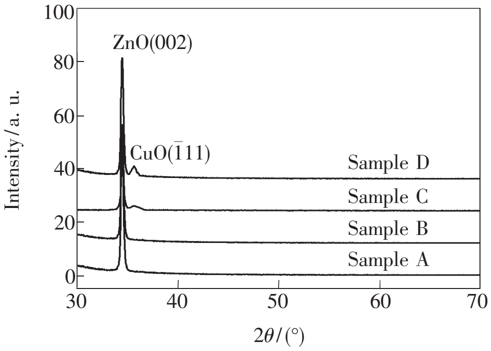

Fig. 1 XRD patterns of sample A ~ D, besides the strong (002) diffractive peaks of ZnO, ($\bar{1}$11) of CuO diffractive peak gradually emerges from sample C to D, indicating that CuO has successfully covered on the core surface and it thickness increase with the increase of treatment time.

A typical SEM image is shown in Fig. 2, which demonstrates that the as-synthesized products consist of high aspect ratio ZnO nanowires. The size of ZnO nanowires ranges from 80 to 200 nm in diameter and 2 μm in length. The smooth surface reveals high quality of the nanowires. After treated with shell layers, the morphologies of the nanowires remain nearly the same with those of the as-synthesized one from the FESEM observations, which may be the result that the shell is overrun the FESEM resolution.

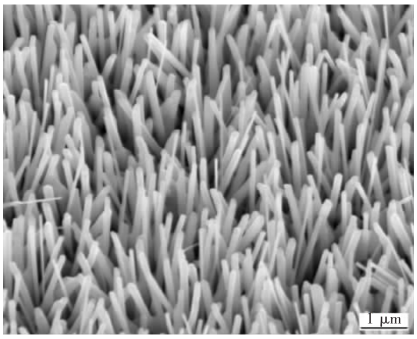

Fig. 2 FESEM image of the as-synthesized ZnO nanowires, the image is tilted 30°, the length of the nanowires is about 2 μm with diameter in the range of 80 ~ 200 nm.

To determine the shell thickness and probe the internal structure of the composite systems as a function of CuO coverage, TEM techniques are employed. The thickness of CuO shells increase with the treatment time. A representative low magnification TEM image of sample C is depicted on the right part of Fig. 3(a), which indicates the nanowire is core-shell structure.

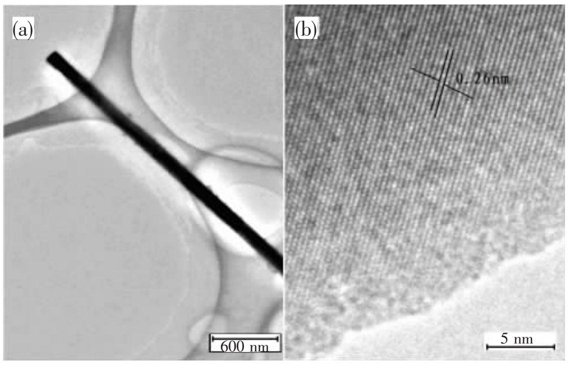

Fig. 3 (a) TEM and (b) HRTEM images of sample C. The HRTEM image of sample C illustrates a well defined interface between ZnO core and CuO shell is observed, the ZnO core is single crystal with well resolved lattice fringes, whereas the shells are polycrystalline CuO.

The HRTEM image of sample C is shown in Fig. 3(b), where a well defined interface between ZnO core and CuO shell is observed, the ZnO core is single crystal with well resolved lattice fringes, the measured lattice spacing is 0.26 nm, corresponding to the (101) direction of wurtzite ZnO, whereas the shells are polycrystalline CuO with thickness of about 3 nm.

Fig. 4(a) shows the evolution of the PL spectra from sample A to sample D. The spectrum of pure ZnO nanowires (sample A) shows a UV near band edge emission centered at 378 nm. When ZnO nanowires are modified by CuO shells, the PL spectra show an interesting evolution both in intensity and peak position of the emissions. The PL intensity increase first (sample A) and reach to the highest value in sample C, but further increase of shell treatment time does not lead to a continuous increase in intensity for sample D. At the same time, the peak position red-shift from sample A to D for about 3 nm. The treatment of ZnO with CuO is a soft process. The thickness of CuO shells increases with the treatment time. At the beginning (from sample A to sample C), the PL intensity of the core/shell nanowires increases, indicating that CuO capping process greatly reduces the number of surface states. When ZnO is treated with Cu^{2+} for short times, Cu^{2+} slowly reacts with ZnO: the Cu^{2+} ions are first absorbed on the ZnO nanowires surface, part of them bind with the surface atoms of ZnO and passivates the surface dangling bonds and the residual are oxided during the following oxygen annealing, forming CuO. Because the CuO layer covered on the surface of ZnO is thin in sample B, the whole electronic structure of the system does not change too much. However, these thin shells are thick enough to passivate most of the dangling bonds on the surface of the ZnO nanowire core, thus removing the surface states which act as carrier trapping centers, leading to the increase of the PL peak intensity, as shown in Fig. 4(a). However, the shells become thick enough for sample C and D, the interruption of increasing in intensity at this time can be attributed to the electronic structures of the core/shell systems. According to the band alignment of the two components, the core/shell structures are typically classified into two types. Type-Ⅰ, in which the conduction band minimum (CBM) and the valence band maximum (VBM) of the core/shell structure is at the same side of the core or shell, so both electrons and holes are localized in the same region. Type-Ⅱ, in which the CBM and VBM are in different sides of the core and shell, so the energy gradient existes on the interfaces and tends to spatially separate electrons and holes on different side of the core/shell[13-15]. In type-Ⅰ core/shell systems with both electron and hole localized in the core region, such as ZnO/CuO, the purpose of the shell is to passivate surface trap states and to protect the excitons from exposure to environmental factors[11]. In type-Ⅱ core/shell systems, the electrons are confined in the core, and the holes are located in the shell, which can lead to some interesting properties. For example, when comparing with either material in isolation, the emission spectrum shifts to lower energies, and the band-gap emission is reduced because of the spatial separation of electrons and holes[16-19]. In our ZnO/CuO core/shell systems, the change in intensity of the PL properties

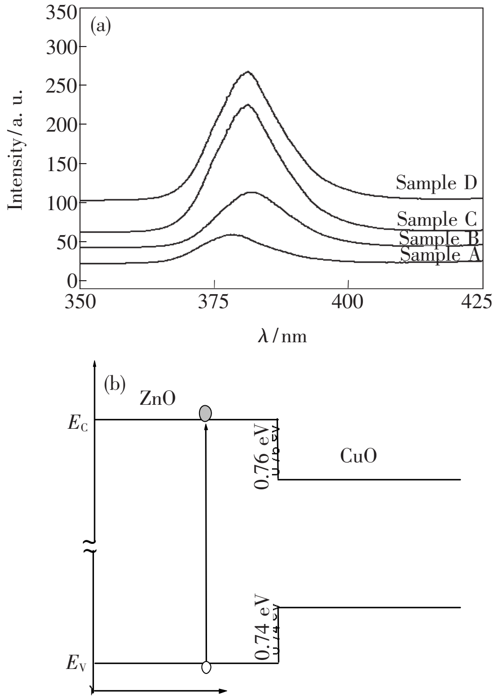

Fig. 4 (a) PL properties of ZnO/CuO core/shell nanowires as a function of CuO shell thickness, the intensity of the band edge emission increase first from sample A and reach to the highest value in sample C, but it stops to continuous increase for sample D, meanwhile the peak position red-shift for about 3 nm from sample A to D; (b) The calculated band alignment.

suggests a transition to type-Ⅰ band alignment, where both electrons and holes are localized in the core region and no carriers transports to the shell from the core. The calculated band alignment is shown in Fig. 4(b), which clearly confirms that the system has a type-Ⅰ band alignment. Therefore, the observed PL change is consistent with the calculated band alignment. The red shift of PL emission of the ZnO nanowires after CuO surface modification is attributed to the fact that the band gap of CuO is narrower than that of ZnO, when Cu^{2+} are adsorbed on the ZnO nanowires surface, translate state ZnCuO may be formed at the interface, which is equal to ZnO doped with Cu and narrows the band gap of ZnO, thus leads to the red shift of the PL emissions.

4 Conclusion

In summary, ZnO/CuO core/shell nanowires are successfully synthesized. The ZnO core is single crystal while the CuO shell is polycrystalline. The effects of the shell thickness on the optical properties are studied in detail. The PL properties of the core/shell structures change with the increase of shell thickness. The increase in intensity of the PL properties at the beginning of the shell growth is due to the decrease of surface states modified by the shell. As the shell is thick enough, a type-Ⅰ band alignment core/shell structures form, where both electrons and holes are localized in the core, which is responsible for the later interruption of increasing in intensity of the PL properties.

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