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Fabrication and Optical Character of High Quality ZnO Microrods

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Abstract We configured reaction solution using zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and methenamine ($C_6H_{12}N_4$) with a certain percentage, magnesium acetate [$Mg(CH_3COO)_2 \cdot 4H_2O$] was added appropriately in the reaction solution. High quality ZnO microrods were prepared on the silicon substrate at 90 ℃ for 24 h by hydrothermal method. Surface morphology and crystal structure of ZnO microrods are analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show the sample presents a rod-like shape with a hexagonal cross sections and typical morphology of wurtzite ZnO. The ratio of length and diameter of the ZnO rod is about 10∶1. And the ZnO microrods grow along [002] direction. Mg ions are not found in the sample, which probably played the role of a catalyst. Photoluminescence (PL) spectrum of ZnO microrods was measured. Room-temperature PL spectrum of the sample shows an UV luminescence peak located at 384 nm, and the FWHM of the emission peak is only 13 nm, intensity of UV luminescence peak is stronger than that of visible luminescence peak, indicating the high quality of the sample.

Key words: ZnO microrods; hydrothermal method; photoluminescence
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1 Introduction

ZnO is a II-VI wide and direct band-gap compound semiconductor material with wurtzite structure. Each Zn atom and four O (oxygen) atoms array by tetrahedron in its crystal structure. The crystal lattice constants are a = 0.325 nm and c = 0.520 nm. ZnO has a large fundamental band gap of 3.37 eV at room temperature, its exciton binding energy (60 meV) and the optical gain coefficient (300 cm^{-1}) are higher than those of other wide band gap semiconductor materials[1,2]. ZnO is an important functional material at the near UV luminescence, optical transparency, electronic conduction and piezoelectricity because of its unique properties. Especially, people have great interests in extensive application of, such as UV laser, biological sensors and solar batteries and so on[3~5]. Now there are many ways to fabricate ZnO with one dimensional structure, relatively mature approaches are magnetron sputtering, hydrothermal method, vapor phase transport method, CVD, PLD[6,7]. Here high quality ZnO microrods were prepared by hydrothermal method and their optical characters were studied in this work.

2 Experiments

ZnO microrods were fabricated by using hydrothermal method. Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and methenamine ($C_6H_{12}N_4$) were configured into 0.01 mol/L reaction solution with molar ratio of 1∶0.5. Appropriate magnesium acetate [$Mg(CH_3COO)_2 \cdot 4H_2O$] were added in the reaction solution. ZnO microrods were prepared on the silicon substrate by hydrothermal method at 90 ℃ for 24 h in a vacuum tank. Higher quality of ZnO large

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microrods on the silicon substrate were observed after adding magnesium ions. The sample was cleaned repeatedly with double distilled water and was dried in nitrogen atmosphere.

Japan HITACHI S-2400 scanning electron microscope (SEM) was employed to examine the morphology of hydrothermal products. The crystal structure of the sample was characterized by D/max-RA X-ray diffraction apparatus (XRD) (made in Japan Ricoh Company, Ltd.) using Cu Kα line of 0.154 18 nm. A JY UV-lamb Micro-laser Raman spectrometer was used to measure the photoluminescence spectrum. A He-Cd laser with pump power of 46 mW and wavelength of 325 nm was used as the excitation source.

3 Results and Discussion

3.1 SEM Analysis

Fig. 1(a) shows a typical SEM image of ZnO product grown by hydrothermal method. It can be seen that the sample presents a rod-like shape with a hexagonal cross section and a typical morphology of wurtzite ZnO. The orientation of ZnO microrods is different and the tops of the microrods are relatively smooth, the length is about 10 ~ 15 μm and the diameter is about 0.5 ~ 1.5 μm, the ratio of length to diameter is about 10∶1. Fig. 1(b) shows the SEM image of ZnO microrods prepared at the same reaction condition without Mg^{2+} in the solution. We can be seen that the sample has not a regular rod-like shape.

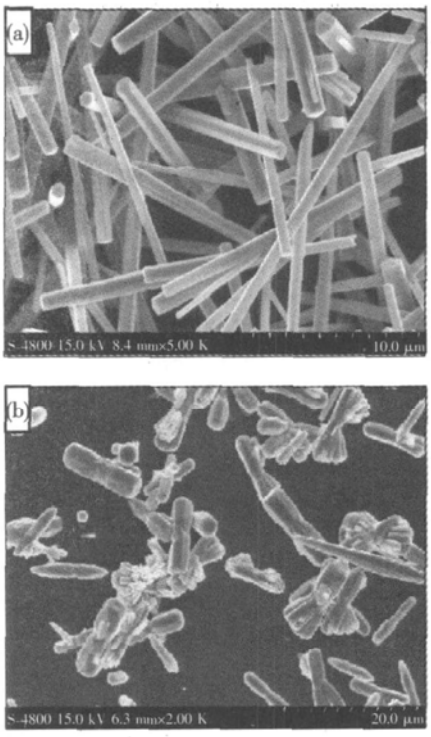

Fig. 1 (a) SEM image of ZnO microrods prepared with Mg^{2+} in the solution; (b) SEM image of ZnO microrods prepared without Mg^{2+} in the solution.

Fig. 2 shows the energy dispersive spectrum (EDS) of the sample. From the spectrum it can be seen that no other element exists except for Zn, O, Si and Al. AlK appears in the spectrum due to using aluminum salver in the experiment. Considering the result of EDS, the pure ZnO has been prepared. It indicates that Mg^{2+} does not enter into ZnO lattice, which probably plays the role of a catalyst. Orbit hybridization mode affects ion's electronegativity considerably. S ingredient in hybridization orbit of Zn is more than that of Mg, so Zn has more ability to attracting electron. Electron cloud of Zn-O is close to Zn ion, increasing the polarity of Zn-O. And the total amount of positive ions and negative ions are changeless after adding Mg^{2+} into the solution. Therefore, the polarity of Zn-O is larger due to the existence of Mg^{2+}, which results in that Zn ions attract electrons in the solution more easily. Consequently, the big microrods were produced[8].

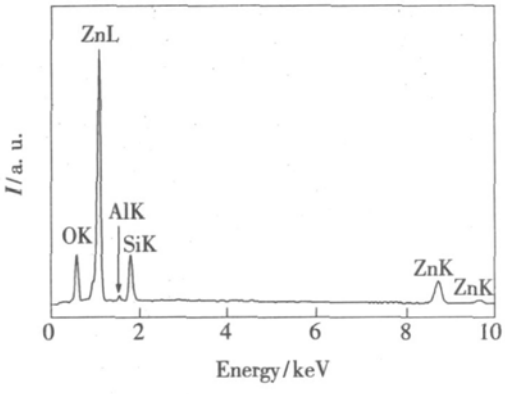

Fig. 2 EDS spectrum of ZnO microrods.

In the growing process of ZnO microrods, zinc acetate provides Zn^{2+}, methenamine hydrolyzes into NH_4^+ and OH^- in aqueous solution. Zn^{2+} and OH^- reacts to produce $Zn(OH)_2$ colloid and further, come into being $Zn(OH)_4^{2-}$ which is called growth unit under alkaline condition. Zn^{2+} ion is at the center of this minus coordination compound tetrahed-

ron, OH^- ions are at the four vertex angles of the tetrahedron. After the solution reaching saturation, hexagonal structure unit is formed by $Zn(OH)_4^{2-}$ reciprocal coalescent through dehydration. The eventual formations are crystal particles. The unit growing process can be expressed as[9]:

$$(CH_2)_6N_4 + 10H_2O \rightarrow 6HCHO + 4NH_3 \cdot H_2O$$

$$NH_3 \cdot H_2O \leftrightarrow NH_4^+ + OH^-$$

$$Zn^{2+} + 2OH^- + 2H_2O \rightleftharpoons Zn(OH)_4^{2-} + 2H^+$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

3.2 XRD Analysis

Fig. 3 shows the X-ray diffraction spectrum of the sample. In comparison with JCPDS standards chart of ZnO powder diffraction patterns, no other diffraction peak appears in the figure, and ZnO hexagonal crystals are the only products. From the figure, it can be seen that two strong peaks present in the $2\theta = 33.242°$ and $34.689°$, respectively. The corresponding crystal planes index are (100) and (002). ZnO crystal lattice constants are calculated, the results are $a = 0.323$ nm and $c = 0.517$ nm. They are a little bit smaller than those of ZnO powder ($a = 0.325$ nm and $c = 0.520$ nm), it is due to the structural difference between microstructure and powder. From the XRD spectrum it can be seen that the (002) peak is the strongest and the diffraction angle is $2\theta = 34.689°$. This shows that the growth of ZnO microrods have obvious (002) preferred orientation.

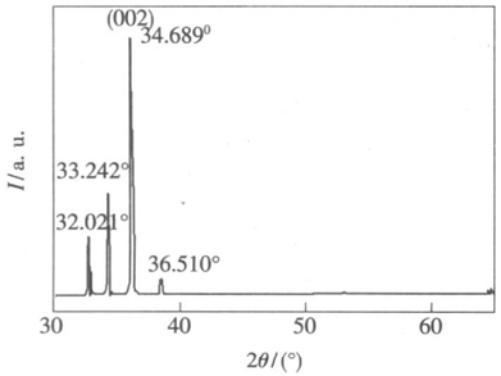

Fig. 3　XRD spectrum of ZnO microrods

3.3 PL Spectrum

Fig. 4 shows the photoluminescence spectrum of the sample measured at room temperature. There is a strong UV luminescence peak at 384 nm, and the FWHM of the emission peak is only 13 nm, which attributes to exciton recombination. Another weak visible luminescence peak is also observed, which comes from the defects of oxygen vacancy and zinc vacancy. Intensity of UV luminescence peak is stronger than that of visible luminescence peak, it indicates that the quality of the sample is very good.

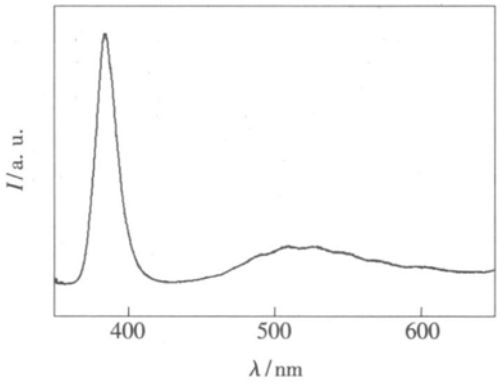

Fig. 4　PL spectrum of ZnO microrods

4　Conclusion

By hydrothermal method, we prepared reaction solution with zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and methenamine($C_6H_{12}N_4$), appropriate magnesium acetate [$Mg(CH_3COO)_2 \cdot 4H_2O$] was added in the reaction solution. The results show that quality of the sample is better than that of ZnO produced without Mg ions in the solution. From SEM photos, we can observe that most ZnO microrods are single, the ratio of length to diameter of ZnO rod is about 10∶1. XRD spectrum indicates that the ZnO rod is hexagonal cross section structure with (002) preferred orientation. Magnesium ions are not found in the product, which probably play the role of a catalyst. PL spectrum of the sample shows only one UV luminescence peak at 384 nm, and the FWHM of the emission is only 13 nm, intensity of UV luminescence peak is stronger than that of visible luminescence peak, the quality of the sample is very good.

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高质量 ZnO微米棒的制备及其光学性质

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摘要: 利用水热法制备 ZnO微米棒。醋酸镁[$Mg(CH_3COO)_2 \cdot 4H_2O$]、醋酸锌[$Zn(CH_3COO)_2 \cdot 2H_2O$]和六次甲基四胺($C_6H_{12}N_4$)以一定比例配置成反应溶液,把反应溶液加热到 90 ℃,反应时间为 24 h,能够在硅衬底上生长高质量的 ZnO微米棒。用扫描电镜(SEM)和 X射线衍射仪对 ZnO微米棒的晶体结构和表面形貌进行了分析,结果表明,样品为细长条棒状结构,呈现六方纤锌矿结构,长径比可达 10∶1,并且在[002]方向择优生长。在样品中并未发现镁离子,它有可能扮演着催化剂的角色。对 ZnO微米棒的光致发光性能进行测量,由 PL光谱分析可知,样品在 384 nm处有一个紫外发光峰,半峰全宽为 13 nm,紫外发光峰强度比可见发光峰强度大的多,样品的质量较好。

关 键 词: ZnO微米棒; 水热法; 光致发光

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