New doping technique of Mn Activator on ZnS Host for Photoluminescence Enhancement

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Abstract: Triple layers structure of SiO_2/ZnS:Mn/ZnS was synthesized by using ion substitution and chemical precipitation method. Each layer thickness was controlled by adjusting the concentration of manganese (II) acetate ($Mn(CH_3COO)_2$) and tetraethyl orthosilicate (TEOS). The structure and morphology of prepared phosphors were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microscopic analyzer (EPMA). Photoluminescence (PL) properties of ZnS with different layer thickness and amount of Mn activator were analyzed by PL spectrometer. PL emission intensity and PL stability .were analyzed for evaluating effects of Mn activator.

1. Introduction

Zinc sulfide (ZnS) is a wide band gap semiconductor with E_g of 3.66 eV at room temperature. As traditional phosphors, ZnS and doped-ZnS show various luminescence properties such as photoluminescence (PL), electroluminescence and thermoluminescence. Therefore, they have been widely used in flat-panel display, electroluminescence devices, infrared windows, sensors, and lasers. The PL of metal ions such as Cu, Co, Mn, Eu and Tb doped ZnS nanomaterials has been investigated. Many people have prepared ZnS:Mn particles by co-precipitation method, but Mn^{2+} ions are not easily doped into the lattice of ZnS. So we try new challenging replacement method coating ZnS:Mn layer over ZnS core, which is designed to enhance luminous efficiency by improving doping of Mn^{2+} ions into ZnS lattice. Because of the existence of oxygen in application environment, the surface of ZnS phosphors can be oxidized into ZnO dead layer, which results in their fast degradation. The surface coating, and encapsulation of phosphors will be used to reduce the surface dead layer thickness and passivating surface recombination centers. As the result of many efforts, thermal and chemical stability of phosphors were improved. Inorganic coating layer also increase PL intensity by increasing the distance between Mn^{2+} ions and surface non-radiative centers. Silica is expected to be one of the candidates for coating because it has energy band gap larger than ZnS, and the wide band gap layer can reflect electrons generated by the incident electron beam from defective high surface region back into phosphors.

In this paper, by some new methods (ion substitution and chemical precipitation), SiO_2/ZnS:Mn/ZnS phosphors were prepared as a new structure. Effect of raw materials ratio on the structure and morphology of prepared phosphors were investigated. Effect of layer thickness on PL intensity was also analyzed.

2. Experimental Procedure

2.1 Specimen Preparation

0.01mol $Zn(CH_3COO)_2$, 0.02mol sodium acetate and a certain amount of sodium polyphosphate ($Na_5P_3O_{10}$) were dissolved in distilled water (50 ml), and then 0.01mol Na2S were added dropwise to the beaker. After 30 min, $Mn(CH_3COO)_2$, Na_2S and $Zn(CH_3COO)_2$ solution were also added dropwise at 30 min interval, respectively. With constant stirring for 4h, white precipitates of ZnS:Mn/ZnS particles was formed as a result. During silica coatings on ZnS:Mn/ZnS phosphors were fabricated by the chemical precipitation method, TEOS as the precursor was introduced into suspended phosphors. The resulted mixture was put into water bath of 80±2 ℃ and neutralized to pH 5.0±0.5 by 0.01 mol/l diluted hydrochloride acid solution addition. Keep stirring for 12 h, coated phosphors were dried at 100～110 ℃ for 12 h.

The crystalline phase samples were determined by X-ray diffraction (XRD, Cu K_, 40 kV, 60 mA, SIEMENS D/max-5000). The morphology of coated phosphors was observed by scanning electron microscope (SEM, JSM 5410). The PL spectrums were recorded by LS-45.

2.2 XRD

In order to check the effect of silica coating layer on ZnS crystallinity, the XRD curves of ZnS, ZnS:Mn/ZnS and SiO_2/ZnS:Mn/ZnS phosphors were recorded and indicated in Fig.1. Three diffraction peaks were corresponding to (1 1 1), (2 2 0) and (3 1 1) planes of the cubic crystalline zinc sulfide, respectively. It could be observed that the XRD curves of these phosphors are very similar. Phosphors coated with silica showed decreased intensity of diffraction intensity first but after annealing showed crystallinity of ZnS. There was no additional peak observed corresponding to silica,

because the layer of silica is amorphous.

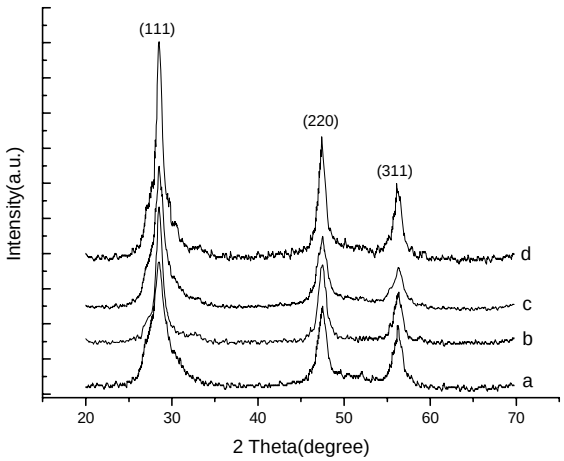

Fig.1. XRD pattern of (a)ZnS, (b)ZnS:Mn/ZnS, SiO_2/ZnS:Mn/ZnS (c)before and (d)after annealed at 500 ℃.

2.3 PL

Figure 2 gives the emission spectra of samples excited at 305 nm. It can be seen that the $4T_1 - 6A_1$ emission of Mn^{2+} ions is at～590 nm, and the intensity of the 590 nm emission of the coated phosphors is seven times that of the uncoated phosphors. The emission peak centered at～400 nm is attributed to the self-activated emission caused by Zn vacancies in the lattice.

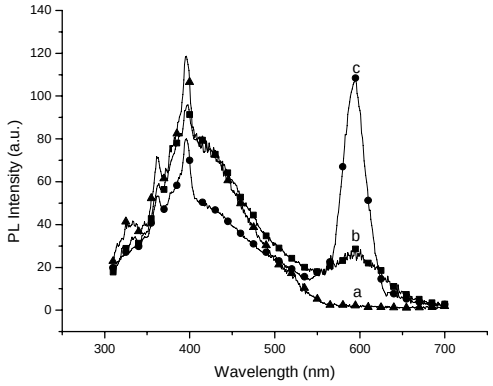

Fig.2. PL spectra of (a)ZnS, (b)ZnS:Mn/ZnS, (c) SiO_2/ZnS:Mn/ZnS.

With an increasing concentration of Mn^{2+} incorporated in the phosphors, the Mn^{2+} emission intensity increases while intensity of blue emission decreases (Fig. 3). PL spectra peak of SiO_2/ZnS:Mn/ZnS were shift from 592nm to 598nm according to Mn^{2+} addition. Peak shift of about 6 nm at higher Mn^{2+} concentration may be due to pair formation of Mn^{2+} ions. Usually due to magnetic interactions between neighboring Mn^{2+} ions, emission peak of magnetically coupled pair is observed to be shifted to the right direction. As a result, it was found that according to increase of Mn^{2+} concentration, emission intensity increased. Peak (d) in figure 3 showed maximum value when content of Mn^{2+} doping was 8%. If Mn^{2+} concentration continued to increase, namely more than 8%, emission intensity showed rather decreased.

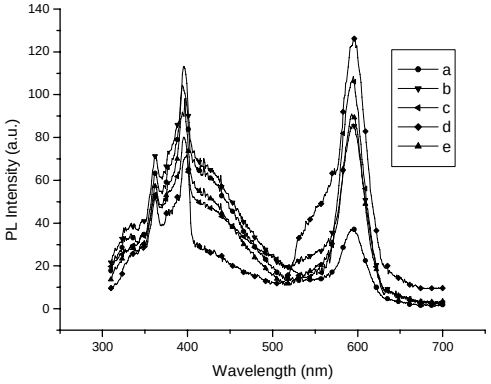

Fig.3. PL spectra of SiO_2/ZnS:Mn/ZnS with varying amounts of Mn^{2+} concentration (a: 2%, b: 4%, c: 6%, d: 8%, e: 10%).

3. Conclusion

A new challenging replacement method for coating ZnS:Mn layer over ZnS core, which is designed to enhance luminous efficiency by improving doping of Mn^{2+} ions into ZnS lattice were synthesized successfully as a form of SiO_2/ZnS:Mn/ZnS. After 2hr annealing treatment, sphalerite structure of ZnS could be confirmed by XRD results, which means zinc blend were obtained and peak intensity of blend increased after annealing. With adjusting thickness ratio of three layers, strong peak intensity could be obtained. Optimum layer thickness of phosphors for strong PL intensity was fabricated at the molar concentration ratio of Zn: Mn: SiO_2 =100: 8: 20 (20%SiO_2/20%ZnS:Mn/60%ZnS).

References

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