

SiO₂/ZnS:Cu/ZnS Triplex Layer Coatings for Phosphorescence Enhancement

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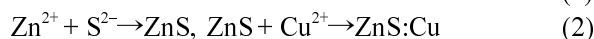
Abstract

The objective of this study is to coat the SiO₂ layer uniformly on the ZnS:Cu phosphors by using Sol-Gel method. From results of SEM micrographs observation, XRD and XPS analysis, it could be confirmed that SiO₂ layer was relatively well coated on ZnS:Cu particles. Ag₂S was used as a decoding chemical to analyze the dense and uniform coating performance of SiO₂ layer on phosphor particles. It could be concluded that phosphors synthesized from our two step replacement method showed strong blue peak comparing to other method and rather weak green peak also. Obtained particle size of phosphors were about 20nm diameter. Luminescence properties of the phosphors were examined by photoluminescence spectra at the excitation wavelength of 270 nm.

Keywords: Silica, ZnS:Cu phosphor, SiO₂/ZnS:Cu/ZnS Coating, Luminescence, Sol-Gel synthesis

1. Introduction

As a wide band gap semiconductor, zinc sulfide (ZnS) which is one of important source for EL (electro luminescence) phosphors such as copper-activated zinc sulfide (ZnS:Cu) phosphors has been surveyed energetically in recent years. As a results, ZnS:Cu phosphors have been widely used in the flat-panel display, electroluminescent devices, infrared windows, sensors, and lasers etc^{1,2)}. Many people have prepared ZnS:Cu particles by co-precipitation method^{3,4)}, which is a common and simple chemical method. However, Cu²⁺ ions are not easily doped into the lattice of ZnS by co-precipitation method due to the solubility product constant of CuS is much smaller than that of ZnS. The solubility product constant of CuS is only 6.0×10⁻³⁶ while that of ZnS is 2.5×10⁻²², so CuS particles are deposited earlier than ZnS, which results in the low luminous efficiency of the prepared ZnS:Cu particles (reaction (1)).



So we tried new challenging replacement method which is designed to enhance luminous efficiency by improving Cu²⁺ ions into ZnS lattice (reaction (2)). By using the reaction (2), we tried fixing ZnS crystal structure first then coating ZnS:Cu layer over ZnS core which means to enhance luminous efficiency with maintaining ZnS structure as it was.

Another unsolved problem is phosphors found to be unstable when EL devices are used in moisture and other atmospheric conditions. To solve stability of ZnS:Cu/ZnS phosphors, many researchers⁵⁻⁸⁾ have tried to enhance the dispersion and stability of ZnS:Cu phosphors by changing synthesis conditions to improve crystallinity and control the optimum size of phosphor particles, namely by using different fluxes, different concentrations of activators and co-activators. However, still results are unsatisfactory. Usually coating of SiO₂^{9,10)}, Y₂O₃¹¹⁾, TiO₂¹²⁾, ZnO¹³⁾ etc. layers on phosphors were suggested for making phosphors stable in moisture or resistant to electron bombardment. Also, thin oxide layer coating on the surface of phosphor particles is suggested to enhance the chemical stability of sulfide phosphors for luminescent enhancement as well as an improved resistance to

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electron bombardment. We also tried SiO₂ layer coating for SiO₂/ZnS:Cu/ZnS triplex layer coatings to obtain transparent, hard and highly resistant to moisture and chemical deterioration.

In this paper, shell/core structure of ZnS:Cu/ZnS phosphor was prepared by replacement method in colloid way by two step process, and then finally we tried to coating SiO₂ layer on them by using Sol-Gel method. The thickness of SiO₂ layer was controlled by adjusting the TEOS concentration. The morphology, structure as well as PL (photo luminescence) properties of SiO₂-coated ZnS:Cu phosphor particles were investigated.

2. Experimental

Zinc acetate and TEOS were used as Zn and Si sources, respectively. Firstly, TEOS and ammonia solution (25%) were added to 60 ml ethanol. The mixture was stirred to form a clear Sol at 40°C. Secondly, at the condition of magnetic stirring, 0.1 mol/l Zn(CH₃COO)₂ and 0.1 mol/l Na₂S were added dropwise to beaker, in which ethylene diamine tetraacetic acid (EDTA) and sodium acetate mixed solution is existed. Thirdly, Zn(CH₃COO)₂, Cu(CH₃COO)₂ and Na₂S were added dropwise to a beaker respectively. The molar composition of Zn(CH₃COO)₂, EDTA and Na₂S was adjusted as 1:1:1 ratio. Finally, prepared shell/core structure of ZnS:Cu/ZnS particles were added to TEOS Sol for silica coating on surfaces of particles at pH 10 during 24 h. Various samples were obtained at different condition of Zn:Cu molar ratio and different TEOS concentration. Finally every sample was dried at constant 70°C temperature. According to the ratio of Zn:Cu as 100:1, 200:1, 300:1, 400:1 and 50:1, the samples were labeled as S1, S2, S3 S4 and S5. For the sample of S2, according to the TEOS amounts of 0, 3, 5, 7 and 9 ml, the samples were labeled as S(2A), S(2B), S(2C), S(2D) and S(2E) respectively. Designed final shell/core structure of phosphors were composed of three layers: SiO₂/ZnS:Cu/ZnS (Fig. 1). We anticipated

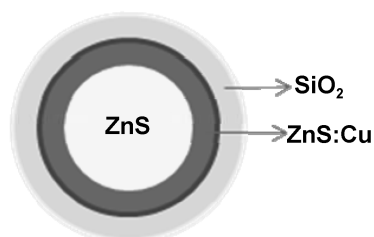


Fig. 1. Designed final shell/core structure of phosphors.

replacement method we used makes it easy both Cu²⁺ and Zn²⁺ to exist uniformly in the lattice for enhancing the luminous efficiency of Cu²⁺.

X-ray diffraction patterns were analyzed for crystallinity examination of phosphors (XRD, CuK α , 40 kV, 60 mA, SIEMENS D/max-5000). The morphology of particles was observed by SEM (JSM 5410). For element analysis of final phosphor and for the chemical state of particle surface determination, MultiLab 2000 X-ray photoelectron spectrometer (XPS) with monochromatic AlK α ($h\nu=1486$ eV) radiation was used. The photoluminescence spectrum (PL) was recorded by LS-45.

3. Results and Discussion

The silica coated thickness and morphology by TEOS has been affected according to various conditions. Through the pre-experimental survey, the concentration of TEOS was most important factor and also reaction time are second important parameters which could affect coating thickness and morphology. In order to investigate the effect of TEOS concentration, the ZnS phosphors were treated with 3~9 ml of TEOS, respectively. Colloid of ZnS:Cu/ZnS particles was added dropwise to different TEOS sol. Fig. 2(A) showed smooth and clean surface of uncoated ZnS:Cu phosphor. It becomes a little bit rough and to start to be coated with silica according to treat with TEOS. Coated thickness of SiO₂ on the ZnS:Cu/ZnS surface was increased according to the increased concentration of TEOS (Fig. 2(B)-(D)). But at 9 ml TEOS adding, owing to excess amount, uncoated SiO₂ fragment appeared (Fig. 2(E)). It seemed to be adequate amount for coating on the phosphor particles at 7 ml concentration of TEOS. A little bit rough but relatively desirable coating was obtained at this condition (Fig. 2(D)).

In order to check the effect of silica layer coating on crystallinity of ZnS:Cu/ZnS, the XRD patterns of uncoated and coated phosphor were examined (Fig. 3). It can be observed that the XRD curves of coated and uncoated phosphors are similar which means SiO₂ coating does not have effect on crystal structure. (111), (220) and (311) are the crystal face index of ZnS structure, which means owing to too small amount of Cu²⁺ ion doping only ZnS peak was appeared. It could be seen that the silica-modified phosphors have only zinc blended structure. There is no additional peak observed corresponding to silica, because the structure of silica layer is amorphous¹³.

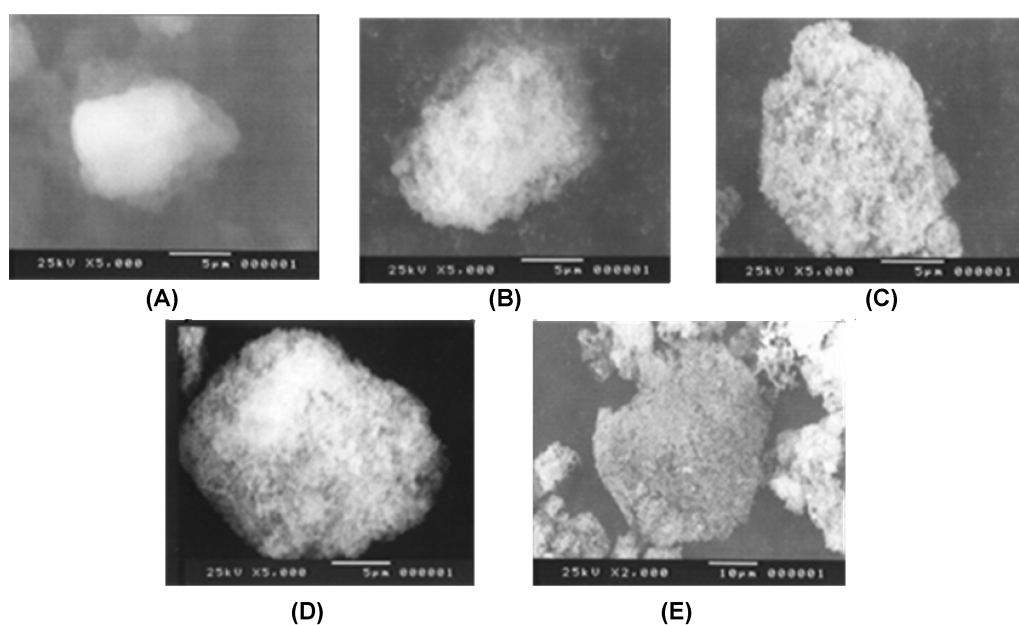


Fig. 2. SEM micrographs of ZnS:Cu phosphors coated with different amount of silica; (A) S_{2A}, (B) S_{2B}, (C) S_{2C}, (D) S_{2D} and (E) S_{2E}.

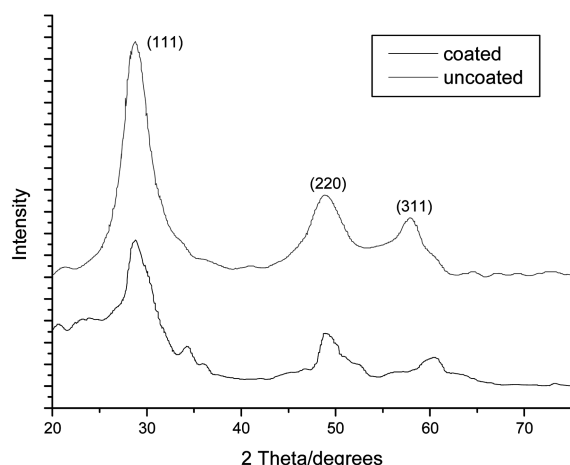


Fig. 3. XRD patterns of uncoated and silica coated ZnS:Cu phosphors.

Table 1. Binding energy of O1s, S2p, Zn2p and Si2p from XPS analysis

Sample	Binding energy (eV)			
	O1s	S2p	Zn2p	Si2p
S _{2A}	531.37	161.73	1021.04	-
S _{2D}	533.68 535.83	161.29	1022.71	104.25

The binding energies of S_{2A} and S_{2D} from XPS analyses are listed in Table 1. The typical Si (2p) peak at 104.25 eV and O(1s) at about 533.68 eV indicates that the sample of S_{2D} is composed by SiO₂ and ZnS. For S_{2A}, the O/S atomic percentage ratio was 21.58/78.42 on the particle surface calculated from the integral area. Unexpected O should be

originated due to the oxygen molecules that adsorbed on the surface of S_{2A} during the sample preparation for the XPS characterization. So, the 531.37eV should be mainly due to the Zn-O bonding. For S_{2D}, two obvious peaks were observed in the O(1s) spectrum at 533.68 and 535.83eV respectively and from the integral area calculation, the O/S atomic percentage ratio was 97.59/2.41. According to X. T. Zu¹⁰⁾, the former should be connected to Si-O and the latter to Zn-O bonds. Compared with that of S_{2A}, the binding energies of Zn2p and O1s of S_{2D} were upward shift. This upward shift could be explained by the increase of the coordination number of Zn and the shortening of the Zn-O bond, which implied that the insertion of Zn²⁺ cations in the tetrahedral sites of the SiO₂ network to form Zn-O-Si linkages¹⁴⁾.

For S_{2D}, the Zn/Si atomic percentage ratio is 56.68/43.32, but it was only 10.72/89.28 on the particle surface calculated from the integral area. It also indicates that ZnS:Cu/ZnS was covered by silica.

From Fig. 4, it can be seen that with increasing Cu²⁺ concentration, the emitting peak of samples increased from 456nm to 467 nm. Also, PL peak intensity increased from 300:1 to 200:1 but after 200:1, peak intensity rather decreased. At 50:1 showed more decreased peak intensity. Obtained PL spectrums (Fig. 4) were complex because of the shell/core structure of SiO₂/ZnS:Cu/ZnS phosphors. According to our experimental results, we got three main emission peaks of PL: 420 nm, 457 nm and

510 nm by using Cu^{2+} ion doping. The peak of 420 nm was ascribed to S^{2-} vacancies³⁾, the internal layer ZnS was used as its source; 457nm(blue) and 510 nm (green) were attributed to Cu, which exist in the second layer, the peak of 510 nm was weak compare to which of 457 nm³⁾. The green peak of Cu was very sensitive to the Cu concentration. In this experiment, we concluded that amount of used Cu ions was too excessive to the green peak, so we got rather weak intensity. As an activator of ZnS, Cu^{2+} concentration showed much effect on the luminescence intensity¹⁵⁾, but luminescence intensity did not increase continuously with the increasing of doped Cu^{2+} concentration. When Cu content exceeds the critical value, the non-radioactive energy transfer between neighboring Cu ions weakens the fluorescence¹⁶⁾. This explanation fit well to our experiment results of Fig. 4. 0.5% means 200:1 condition.

The PL spectra (Fig. 5) showed that S_{2D} (7 ml

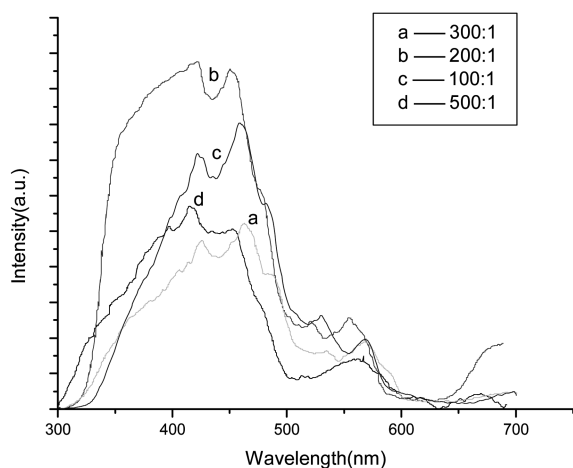


Fig. 4. PL spectrum of ZnS:Cu phosphors coated with SiO_2 according to different ratio of Zn to Cu at 7 ml concentration of TEOS.

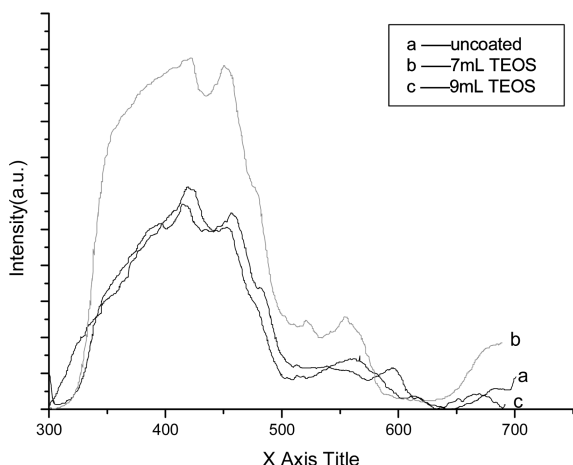


Fig. 5. PL spectra of ZnS:Cu phosphors coated with different TEOS amounts at 200:1 ratio of Zn:Cu.

TEOS) phosphors have much higher emission intensity than those of S_{2A} (uncoated). It means that even at best condition of Fig. 4 (200:1), according to TEOS concentration, peak intensity changed largely. According to nonradioactive transition theory¹⁷⁾, increased emission intensity may be explained that the uniform SiO_2 -shell reduced the surface defects of ZnS spheres which act as the nonradioactive centers of excited holes and electrons. Fig. 5 also shows that, the PL intensities of S_{2E} (9 ml TEOS) are found to be 1~2% lower than that of uncoated phosphor. According to Y. Feng's explanation, it could be guessed that because the light emitted from the phosphor particles is covered and irregularly reflected by the SiO_2 coating, so that the quantity of light escaping from phosphor to outside is reduced, leading to a reduction in PL intensity¹⁸⁾.

PL intensities of coated and uncoated phosphors were compared for 14 days by keeping them in moisture. It was found that the brightness of the uncoated phosphor reduces to almost half to its initial value, on the other hand the coated phosphor showed the almost same PL intensity even after 14 days. This clearly indicates that coated phosphor is stable against moisture. In order to test the stability of silica film (free from pinhole and cracks), the moisture resistance was evaluated with AgNO_3 solution. Although coated phosphor was immersed in the 0.02 mol/l AgNO_3 solution during 30 min, there was no appreciable change of phosphor color. But uncoated phosphor just turned into black within 1 min due to the formation of Ag_2S .

4. Conclusions

Mono dispersed silica-modified ZnS:Cu/ZnS particles could be prepared successfully by our own two step Sol-Gel method. From XRD analysis, it could be seen that the silica-modified phosphors have only zinc blended structure. For $\text{SiO}_2/\text{ZnS:Cu/ZnS}$ triplex layered phosphors, "ZnS:Cu/ZnS particles were added to TEOS Sol for silica coating at pH 10 during 24 h. From XPS analysis, it could be proved that there existed strong interaction between SiO_2 and ZnS. It indicated ZnS:Cu/ZnS surfaces were covered with SiO_2 . It can be seen that with increasing Cu^{2+} concentration, the emitting peak of samples increased from 456 nm to 467 nm. Also, from PL peak spectrums, intensity has maximum value at 200:1 ratio of Zn to Cu at 7 ml TEOS. SiO_2 coated phosphors were found to be stable even in AgNO_3 solution.

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