Effect of nanoscaled SnO_2 coating on ZnS:Mn phosphors under electron irradiation

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Abstract

The luminescence properties of SnO_2-coated ZnS:Mn phosphors are investigated. In the case of photoluminescence, emission intensities show little change when SnO_2 is coated on the surface of ZnS:Mn, while in the case of cathodoluminescence (CL), emission intensities vary depending on excitation energies. In order to determine the luminescence behaviors, surface analyses of the phosphors were performed. Auger electron spectroscopy showed that the width of the SnO_2 layer on the ZnS:Mn phosphor was saturated at approximately 120 nm. Also, X-ray photoelectron spectroscopy indicated that the SnO_2 layers are well formed and saturated when the molar ratios of Sn/Zn are larger than 0.005. These results suggest that the changes in the CL emissions can be attributed to a lowering of the junction barrier.

1. Introduction

The application of surface coatings on display phosphors has proved an effective solution to many of the difficulties and drawbacks inherent in display phosphors. In this regard, to make the feasible application of phosphors in field emission displays (FEDs), it is expected that coating the phosphor surface with a conductive material would increase the cathodoluminescence (CL) intensity. CL properties are expected to improve as a result of decreased phosphor resistivity caused by the surface coating. Also, it has been reported that wide-band oxides, such as SiO_2, WO_3, V_2O_5 and SnO_2, could lead to a noticeable increase in CL intensity [1–4]. However, most studies to date have focused on low-excitation energies, i.e., from hundreds of eV to 1 keV.

It is also thought that a hydrophobic coating may help mitigate aging of phosphors, which are degraded by water absorption. In plasma display panels (PDPs), the luminescence properties of a blue phosphor, such as $BaMgAl_{10}O_{17}$:Eu (barium magnesium aluminate; BAM), are degraded when H_2O is absorbed [5]. Thus, it is thought that a hydrophobic coating on the BAM phosphor may help protect against water absorption.

This paper is focused on the effect of coating ZnS:Mn phosphors with SnO_2 under low and medium energies of electron irradiation. The usefulness of ZnS:Mn phosphors has been explained well in Ref. [6]. The surface coating material, SnO_2, is a good conductor and has high transmittance over the visible light range [7,8]. Thus, coating ZnS:Mn with SnO_2 is expected to reduce the electron charge up on the phosphor, which would result in increased CL intensity under electron irradiation. In the present work, a sol–gel process is used to

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coat the SnO_2 on the phosphor surface. The obtained results indicate that the SnO_2 coating is effective at a medium energy of electron irradiation.

2. Experimental

2.1. Phosphor synthesis

The ZnS:Mn phosphor was synthesized according to the conventional method. The hexagonal phase of ZnS powder (average particle size $= 3–4\,\mu m$) and $MnSO_4 \cdot 5H_2O$ were used as host material and activator, respectively. $ZnCl_2$ and/or NH_4Cl were used as flux materials. The raw materials were mixed in water and dried. After drying, sulfur powder was added to the raw materials to compensate for the sulfur deficiency. Sintering was performed at 900–1100 °C for 2 h in air. The procedure is explained in detail in Ref. [9].

2.2. SnO_2 coating

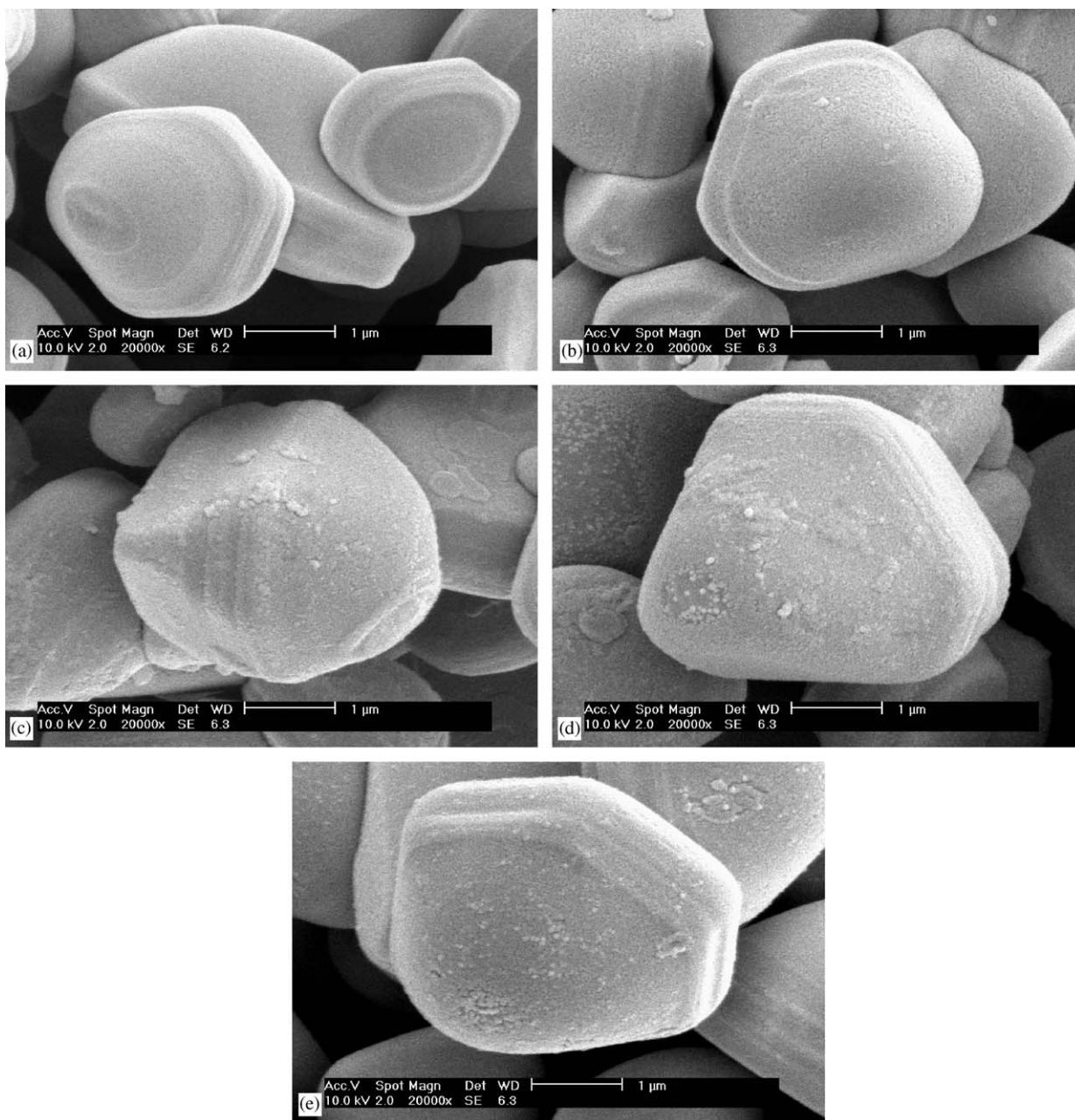In order to make a SnO_2 coating on the ZnS:Mn phosphor, water soluble $SnCl_4 \cdot 5H_2O$ was used as a

Fig. 1. SEM images of ZnS:Mn phosphor and SnO_2-coated ZnS:Mn phosphor: (a) non-coated (as is) sample; (b) Sn/Zn = 0.001; (c) Sn/Zn = 0.005; (d) Sn/Zn = 0.01; and (e) Sn/Zn = 0.01. The scale bar is represented as 1 μm.

precursor. First, a suitable amount of $SnCl_4 \cdot 5H_2O$ was added to H_2O and the resultant solution was stirred for over 1 h. The phosphor powder was then added to the solution by stirring for more than 2 h. In order to precipitate $Sn(OH)_4$ on the phosphor surface, a diluted ammonium solution was used. After filtering, the phosphor was dried at 120 °C. Heat treatment was performed for 1 h at 500 °C to convert the tin hydroxide to tin dioxide [8].

2.3. Measurement of optical properties

In order to investigate optical properties, the photoluminescence (PL) and CL of the ZnS:Mn phosphors were measured at room temperature. The PL was measured using a photon-counting spectrometer (DARSA-Pro) with a Xe-arc lamp operated at 300 W. The CL was measured using a demountable ultra-high vacuum chamber equipped with a laboratory-built CL spectrometer. Measurements of CL were carried out at excitation energies of 300 eV or 3 keV and at beam current densities of 10 or 100 $\mu A/cm^2$. The luminescence measurements were conducted on powder samples. For very low-energy excitation, a W-filament was used as an electron source. In this case, CL was tested at a low excitation energy of 30 eV and a filament current density of an order of 1 mA/cm^2.

3. Results and discussion

Fig. 1 shows secondary electron microscope (SEM) images of the SnO_2-coated ZnS:Mn phosphors. From the figure, it appears that SnO_2 is formed continuously at the molar ratio of Sn/Zn = 0.001. However, as the molar ratio of Sn/Zn is increased, small spots appear on the phosphor surface.

Fig. 2 shows the PL intensities according to the molar ratio of Sn/Zn. In previous studies, the main excitation and emission bands of the ZnS:Mn phosphor were determined to be approximately 356 and 585 nm, respectively [9]. PL intensities of the SnO_2-coated ZnS:Mn phosphors were slightly increased when compared with the non-coated (as is) sample. It is known that the absorption edge of SnO_2 lies at 355 nm [10]. This value is nearly the same as the main excitation of the ZnS:Mn phosphor. Thus, it is thought that emission from the ZnS:Mn phosphor excited with a wavelength of 356 nm is not decreased by the SnO_2 coating. It is believed that the small increases in PL intensities may be caused by surface healing of the ZnS:Mn phosphor, which occurs during the heating process employed to make the SnO_2 coating.

The changes of CL intensities are represented in Fig. 3. The CL intensities are normalized when the non-coated phosphor is scaled as unit. In CL measurements,
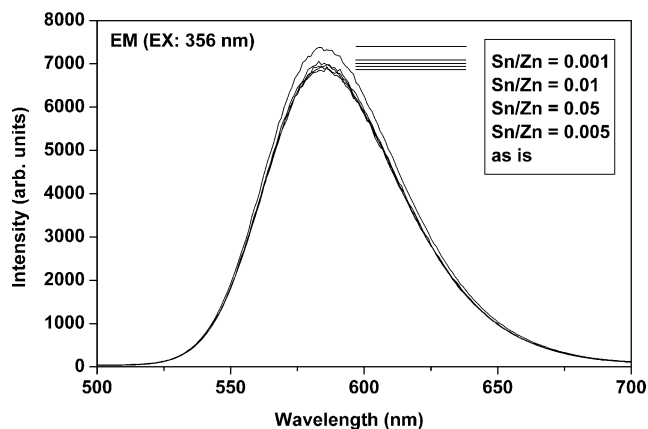

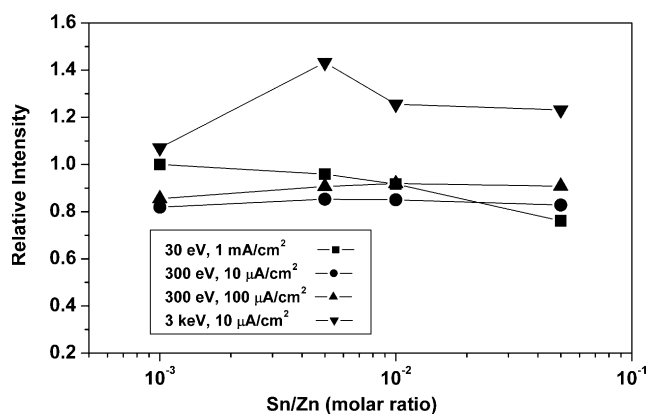Fig. 2. PL intensities varying with the molar ratio of Sn/Zn when excited with a wavelength of 356 nm.

Fig. 3. CL intensities varying with the molar ratio of Sn/Zn under electron irradiation. The irradiation power per unit area on the phosphor surface is kept constant.

the irradiation power per unit area on the phosphor surface is kept constant. When the phosphors are irradiated by excitation energy of 30 eV, the emission intensity is decreased as the molar ratio of Sn/Zn is increased. The emission intensity increases in the case of excitation energy of 300 eV, however, the intensity is smaller than the unit. When the phosphors are excited with excitation energy of 3 keV, CL intensity is increased in all the experimented ratios; the molar ratio of Sn/ Zn = 0.005 shows the maximum CL intensity. The fluctuation of CL intensities excited with excitation energy of 3 keV may be related with the saturation of the SnO_2 coating layer and generation of the small spots, as illustrated in Fig. 1.

As explained previously, three different irradiation energies were used in CL measurements. Interestingly, among the three energies tested, the greatest increase in CL intensities occurs at medium-excitation energy (3 keV). The decreases of CL intensities in the relatively low energies of 30–300 eV could be explained by the

concept of contact electrification [11–13]. According to Ref. [13], the surface charge of SnO_2 is more negative than that of ZnS. Thus, it is thought that when SnO_2 is coated on the ZnS:Mn phosphor surface, the phosphor surface becomes effectively negative due to the coated SnO_2. This negative charge tendency of SnO_2-coated ZnS:Mn phosphors may reduce the CL intensities more than in non-coated ZnS:Mn phosphors under low-excitation energies. The concept of contact electrification appears to be valid under low-excitation energies. However, when the excitation energies increase to 3 keV, the CL intensities of coated phosphors are increased, as shown in Fig. 3. Therefore, the concept of contact electrification is not suitable to explain all the CL properties.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were employed in order to study the features of the coated surfaces in greater detail. Fig. 4 shows depth profiles of phosphor and coating elements obtained from AES. The signal was stopped when the Sn signal disappeared. From the results, the SnO_2 layers appear to have formed on the

ZnS:Mn surface for all the phosphors and the SnO_2 layer appears to be saturated when the molar ratio of Sn/Zn exceeds 0.005. The coated layer is estimated at about 120 nm when the sputtering rate of Ar ion was set to 10 Å/s in the case of the SiO_2 thin film layer.

Fig. 5 shows XPS spectra of activator Mn ions. From this result, it is thought that no change of the electronic state of Mn ions occurs. However, in the case of Sn ions, peaks from $3d_{5/2}$ (at about 487 eV) and $3d_{3/2}$ (at about 496 eV) states increase and become saturated when the molar ratio of Sn/Zn increases, as shown in Fig. 6. The main peak position of the O 1s signal detected from the Zn–O bond is approximately 1.2 eV higher than that of the O 1s signal detected from the Sn–O bond [14]. Also, the O 1s signal was detected from the non-coated phosphor, as indicated in Fig. 7. It is thought that the O 1s signal detected from the non-coated phosphor arises from the Zn–O bond of natural oxidation of phosphor surface. As indicated, the Sn signals increase and become saturated as the molar ratio of Sn/Zn increases. Thus, it is thought that the oxygen bond changes from a Zn–O bond to a Sn–O bond when the molar ratio of
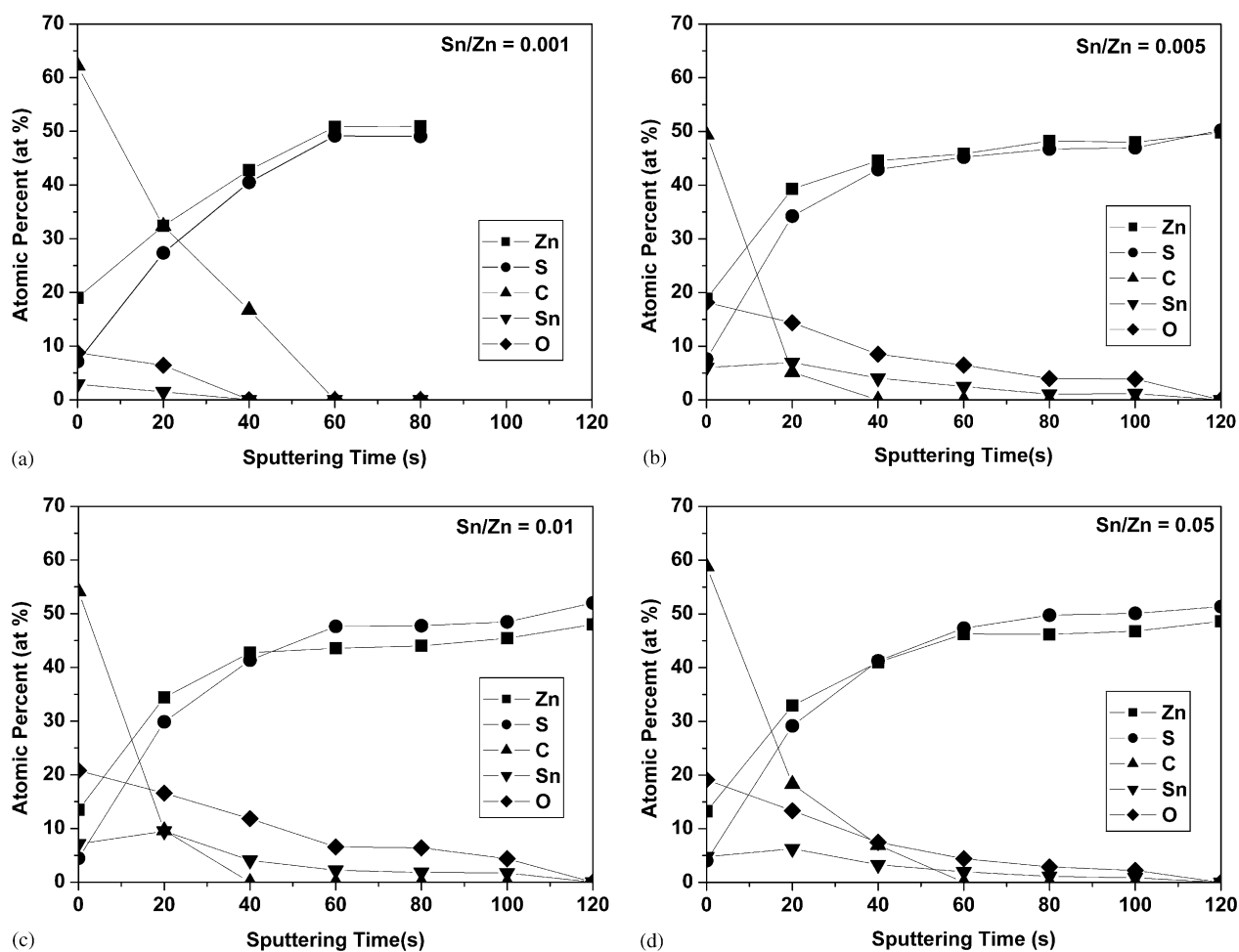

Fig. 4. Depth profiles of phosphor and coating elements obtained from AES: (a) Sn/Zn = 0.001; (b) Sn/Zn = 0.005; (c) Sn/Zn = 0.01; and (d) Sn/Zn = 0.05.
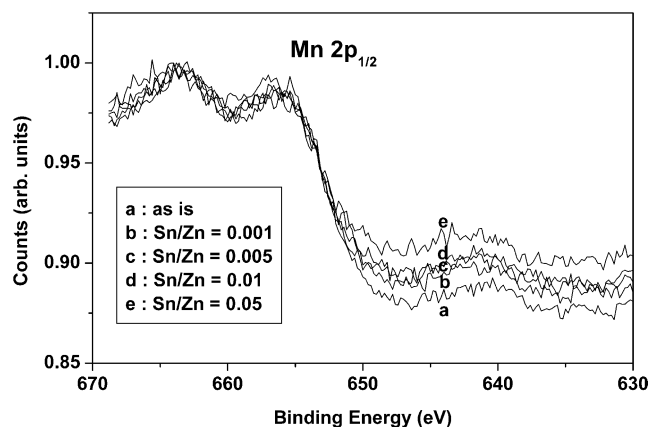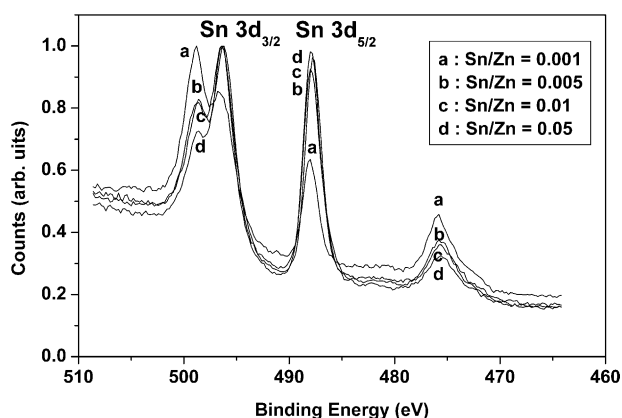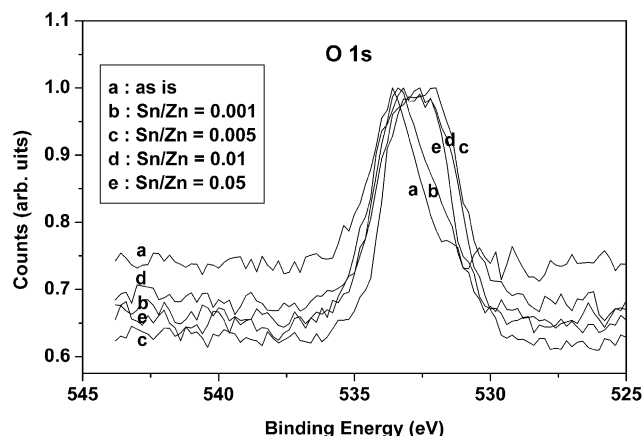
Fig. 5. XPS spectra of activator Mn ions.

Fig. 6. XPS spectra of Sn ions. Peaks from $3d_{5/2}$ (at about 487 eV) and $3d_{3/2}$ (at about 496 eV) states increase and become saturated when the molar ratio of Sn/Zn increases.

Fig. 7. XPS spectra of O ions.

phosphor surface. On the other hand, the band gap energy of SnO_2 and hexagonal ZnS is 3.6 eV [15] and 3.8 eV [16], respectively, at room temperature. It is known that Mn ion-doped ZnS can be effectively treated as a p-type semiconductor [17]. Calculating the virtual acceptor level (E_A) from the bound exciton model, it is estimated at 0.048 eV from the valence band of the ZnS [17]. In this calculation, an energy of BE at 31020 cm^{-1} in Fig. 3 from Ref. [17] and a ZnS band-gap energy of 3.904 eV are used. It is also known that SnO_2 is an n-type semiconductor due to oxygen vacancies [7]. The ionization levels of oxygen vacancies are 0.03 eV for the first ionization and 0.15 eV for the second ionization [7]. Taking this into consideration, full ionization, i.e., the second ionization level is adopted as the donor level of SnO_2 (E_D). Thus, a SnO_2-coated ZnS:Mn phosphor could be thought of as a p–n hetero-junction structure. Although the exact junction structure cannot be predicted with these limited data, it is expected that a semi-quantitative hetero-junction would form when the two materials contact. Fig. 8 shows a schematic representation of an energy band diagram at the phosphor surface. The Fermi level of ZnS (E_{F1}) is located above the E_A and the Fermi level of SnO_2 (E_{F2}) is located below the E_D. When the contact (or coating) is formed, the Fermi level of the whole system will set to be equal and a potential barrier (or junction potential) is expected as a result of the contact. Although the calculation of the exact potential barrier is difficult at present, a rough estimation is possible by using the E_D and E_A levels. From the levels, the potential barrier is expected to be lower than 3.602 eV. Therefore, CL changes at all the excitation energies could be explained
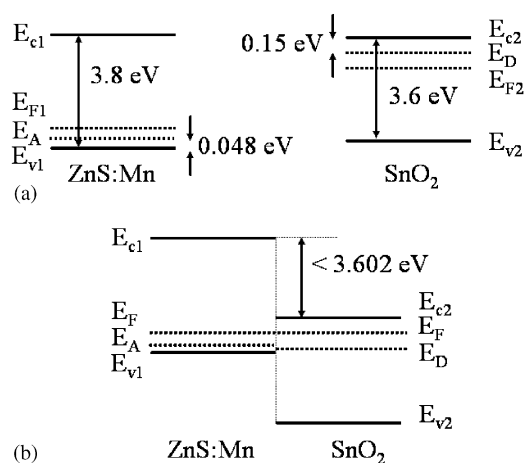

Fig. 8. A schematic representation of an energy band diagram at the phosphor surface: (a) two separated materials and (b) hetero-junction formed by coating. E_{ci}, E_{vi}, and E_{Fi} represent the conduction band, valence band and Fermi level of each material ($i = 1, 2$), respectively. The location of E_{F1} for ZnS is assumed to be above the virtual acceptor level (E_A). In the case of SnO_2, the location of E_{F2} is below the donor level (E_D).

Sn/Zn increases. As such, the variations of CL intensities could be attributed to the coated phosphor surface.

The above results indicate that there is little likelihood that another layer exists between the SnO_2 layer and the

by the concept of a hetero-junction of the SnO_2 layer and ZnS:Mn phosphor.

Once electron irradiation commences, a negative bias is effectively applied at the SnO_2 side in the p–n junction structure. The effective bias on the junction structure can be estimated by the following equation:

$$V_{eff} = \frac{R_{ph}}{R_{ph} + R_{vac}} V_{app},$$ (1)

where R_{ph} is the resistance of phosphor, R_{vac} is the resistance of vacuum, and V_{app} is the excitation energy divided by electron charge. If the values are taken from those used in Refs. [7] and [18], that is, $R_{ph} \leqslant 10^4$ ohm and $R_{vac} \geqslant 10^6$ ohm, then the order of magnitude value of the V_{eff} is reduced from 10^{-3} to $10^{-2} \cdot V_{app}$. In this calculation, the resistance of SnO_2 is adopted as the value of R_{ph} because of the surface coating of the phosphor. From the results, the junction barrier is estimated to be lower than 3.602 eV, as shown in Fig. 8. Thus, the junction barrier will be detectably decreased by the aid of excitation energies if the excitation energies are larger than the order of keV. Therefore, it is conceivable that the CL intensities of SnO_2-coated ZnS:Mn phosphors are increased at an excitation energy of 3 keV.

4. Summary and conclusion

In this paper, the luminescence properties of SnO_2-coated ZnS:Mn phosphors were investigated. The SnO_2 coating was saturated when the molar ratio of Sn/Zn was larger than 0.005. In PL measurements, the PL intensities were increased when SnO_2 was coated on the surface of ZnS:Mn, while the CL intensities are varied depending on the excitation energies. Considering all the results, including AES and XPS analyses, it is thought

that a hetero-junction structure is formed at the SnO_2 and ZnS phosphor surface and that CL intensities increase at 3 keV as a result of lowering the junction barrier.

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