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Electroluminescence from CdSe microcrystals-doped indium tin oxide thin films

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When the DC voltage (4 V cm^{-1}) was applied to the CdSe microcrystals doped indium tin oxide (ITO) thin film prepared by RF-magnetron sputtering method, the red colour luminescence was observed. The luminescence spectrum had two peaks of about 710 and 880 nm, and the ascending tail at longer than 900 nm. It was considered that the luminescence at 710 and 880 nm is electroluminescence, which may be attributable to the surface defect of CdSe microcrystals. © *1998 Kluwer Academic Publishers*

1. Introduction

Electroluminescence (EL) is one of the electron transfer processes, which occurs upon the application of electric field to the specific materials. EL has been studied for organism [1] and semiconductor-based materials [2–4]. Among these studies, Colvin *et al.* [4] reported EL from a heterojunction structure such as the indium tin oxide/semiconductor poly(paraphenyl vinylene)/layered CdSe microcrystals/Mg electrode. The luminescence changed in colour from red to yellow, depending on the particle size of CdSe microcrystals. Then, they ascribed the change of band gap energy of CdSe, which is induced by quantum size effect, to the colour change.

It is considered that semiconductor microcrystals-doped conducting thin films also have the possibility to generate the luminescence of various wavelengths, which can be changed by selecting the species of semiconductor and its particle size. Further, such thin composite films are prospective because they are easily prepared by the RF-magnetron co-sputtering method which has been extensively used in the author's laboratory for making microcrystals-doped glass films with large optical non-linearity [5–7]. From such points of view, Matsuoka *et al.* [8] made CdSe microcrystals-doped indium tin oxide film by the sputtering method, from which red colour luminescence was observed during the application of d.c. voltage. The associated experimental facts that there was a threshold voltage for the luminescence and the luminescence colour was not changed if the applied voltage was changed, led them to the preliminary conclusion that the luminescence should be related to the electron transfer between different energy states. However, their luminescence spectra covering only the range from 400 to ∼ 850 nm has limited the further discussion.

The present work is an extension of the previous one [8] to the same kind of the composite film but including CdSe microcrystals made intentionally larger, and will report the luminescence spectrum measured up to 1000 nm in order to proceed more extensively the argument on the luminescence process.

2. Experimental procedure

CdSe microcrystals-doped ITO (indium tin oxide) thin films were prepared by the RF-magnetron sputtering method. A CdSe (purity: 99.99%) pellet of 10 mm in diameter and 5 mm thick was mounted on an ITO plate (Sn: 5 wt %, purity: 99.99%) of 90 mm in diameter and 5 mm thick to prepare a composite target [9]. The surface area ratio of the CdSe pellet to ITO plate was 1.6%. The sputtering power was 200 W, and the substrate temperature was 200 °C. The sputtering gas used was a high-purity argon gas (purity: 99.99% up), and the gas pressure was set to 5.0×10^{-1} Pa. The distance between electrodes was 50 mm. The adopted substrate was SiO_2 glass (Asahi Glass Corporation), and the sputtering time was 1 hr.

The prepared thin films were examined by X-ray diffraction (XRD) technique using Ni-filtered CuK_α radiation in order to characterize the included microcrystals. The measurement was conducted from $2\theta = 10$–70° at room temperature. The chemical composition of the CdSe in the films was determined by X-ray photoelectron spectroscopy (XPS) using MgK_α radiation as an X-ray source. Xe sputtering for 30 s was carried

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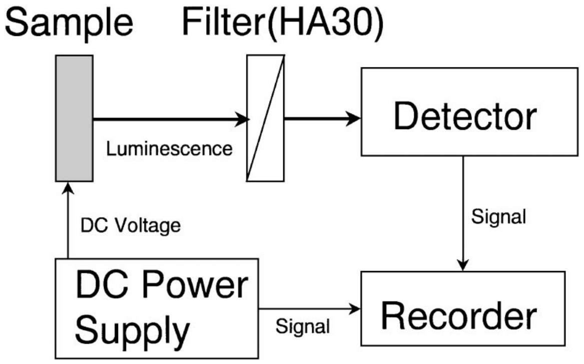

Figure 1 Schematic illustration of luminescence relaxation measurement.

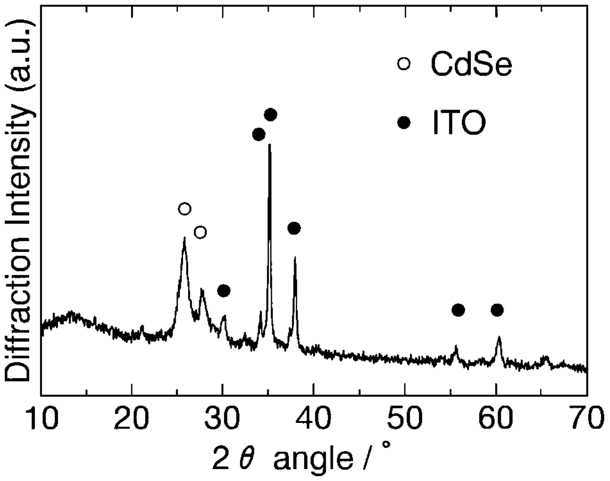

Figure 2 XRD pattern of as-deposited thin composite film prepared with the substrate temperature of 200 °C, relative CdSe/ITO surface area ratio of 1.6%, and the sputtering power of 200 W.

out prior to the measurement to remove any surface contamination. Binding energy of Cd3d$_{5/2}$ and Se3d electrons, normalized to C1s peak, was measured. The measurement of optical absorption spectra was performed from 200 to 2000 nm using a spectrophotometer (JASCO V-570) at room temperature. The luminescence spectra were measured from 550 to 950 nm at room temperature. For the luminescence measurement, two electrodes with a separation of 10 mm were attached to the film by painting silver paste and d.c. voltage was applied across these two electrodes. The luminescence relaxation was measured using a system schematically illustrated in Fig. 1, with and without HA30 filter (HOYA Corporation).

3. Results

The XRD pattern of as-deposited thin film prepared with the substrate temperature of 200 °C, relative CdSe/ITO surface area ratio of 1.6%, and the sputtering power of 200 W is shown in Fig. 2. The relatively broad diffraction peaks at about $2\theta = 26$ and 28° indicated by open circles can be assigned to CdSe with a zincblende-type structure. The other sharp diffraction peaks are assigned to ITO. The average particle size of microcrystals calculated using Sherrer's equation was 9 nm.

Fig. 3a and b show the XPS spectra of Cd3d$_{5/2}$ and Se3d for the same film as one shown in Fig. 2. The peak position of Cd3d$_{5/2}$ corresponds with Cd in CdSe, and any peak corresponding to metallic Cd, Cd in CdO or in other oxidation states is not observed. Se3d peak position also corresponds with Se in CdSe, and no peak for metallic Se, Se in SeO$_2$ or in other oxidation states is observed.

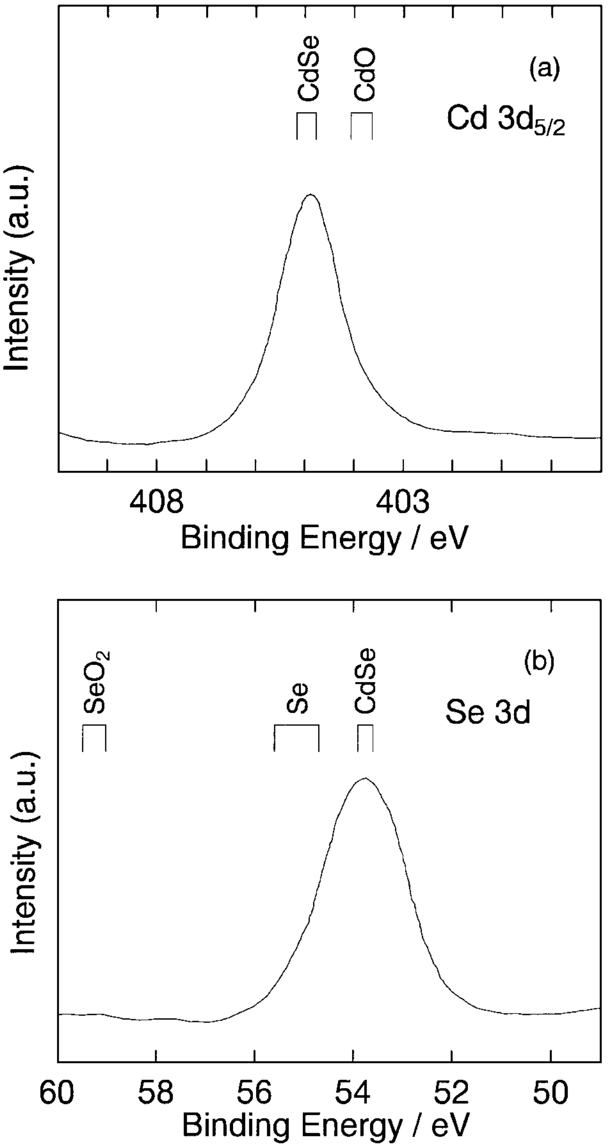

Figure 3 XPS spectra of (a) Cd3d$_{5/2}$ and (b) Se3d for the CdSe microcrystal-doped ITO film.

Fig. 4 shows the optical absorption spectra of the composite film and the pure ITO thin film prepared by the same sputtering condition. The absorption at longer than 1000 nm in the composite film is due to the plasmon resonance of ITO, which is also observed in pure ITO film. For the absorption on the short wavelength side, the absorption edge of the composite film is at longer wavelength than that of the pure ITO film.

The luminescence spectra of the composite film are shown in Fig. 5 when d.c. voltage of 2, 3 and 4 V cm^{-1} is applied, respectively. No luminescence is observed when 2 V cm^{-1} is applied. When 3 V cm^{-1} is applied, a weak luminescence peak appears at 800∼900 nm, but is not visible to the naked eye. At the applied voltage of 4 V cm^{-1}, an intensive luminescence peak emerges at 700∼750 nm, with the peak at 800∼900 nm becoming larger. The film exhibited red colour. The peaks at

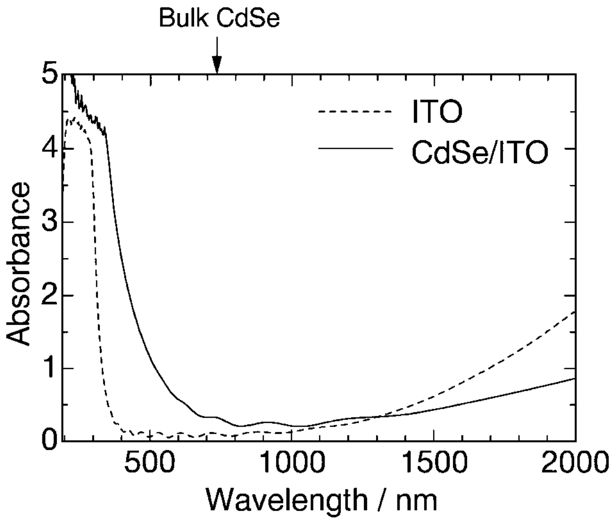

Figure 4 Optical absorption spectra of the CdSe microcrystal-doped ITO film (solid line) and the pure ITO thin film (broken line).

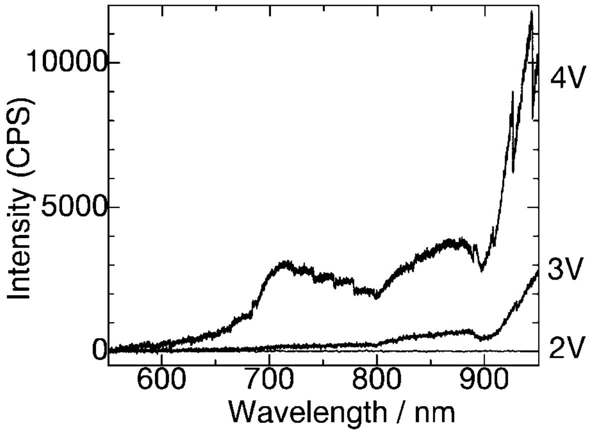

Figure 5 Luminescence spectrum of the film measured under the application of 2, 3 and 4 V cm^{-1} d.c., respectively.

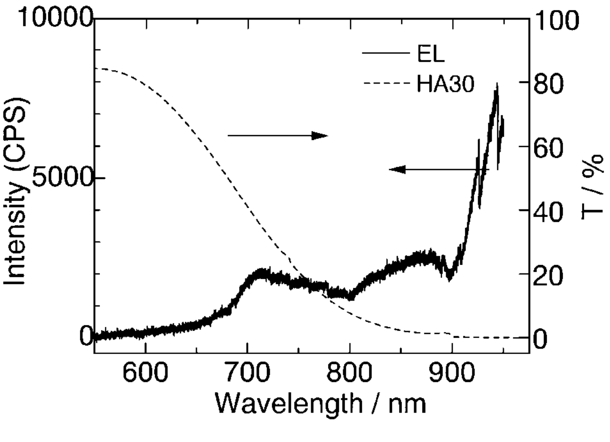

Figure 6 Luminescence spectra of the film measured under the application of 4 V d.c. (solid line), and transmittance spectrum of HA30 filter (broken line).

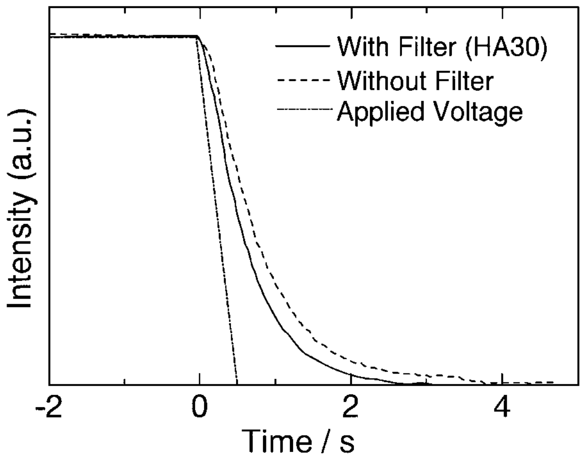

Figure 7 Relaxation spectrum of luminescence under the application of 4 V d.c. with HA30 filter (solid line) and without filter (broken line). Broken line stands for the decay of voltage.

$\sim$ 710 and 880 nm increased in intensity almost without changing their position as the applied voltage was increased to 10 V cm^{-1}. As the applied voltage increased from 0 to 10 V, the electric current increased from 0 to 10 A; however the resistivity of the composite film was kept almost constant at 1 Ω cm^{-1}.

The relaxation or decay of the luminescence was, then, measured with or without using cut-off filter of which transmission spectrum is shown in Fig. 6 together with the luminescence spectrum obtained at 4 V cm^{-1}. It is seen from Fig. 6 that by using the filter, one can isolate the relaxation phenomenon of 710 nm peak from that of other peaks above about 800 nm. The results of the luminescence relaxation measured with or without filter are given in Fig. 7, in which the decay curve of d.c. voltage after turning off is also shown. It is noted that the relaxation of the luminescence peak at 710 nm measured with the filter is faster than that of whole luminescence measured without the filter, suggesting the different origin of the former peak from the others.

4. Discussion

From the result of XRD measurement shown in Fig. 2, it is found that no other crystalline species than CdSe and ITO are contained in the present composite film. On the basis of XPS results shown in Fig. 3, it is found that almost all Cd atoms are combined with Se atoms, and vice versa, as any other chemical state of Cd and Se other than that in CdSe compound is not detected. The broadness of the XRD peak assigned to CdSe tells us that the crystal size of CdSe precipitated in the ITO film is as small as $\sim$ 9 nm, but is a little larger than previously prepared one ($\sim$ 3 nm). Eventually, the composite film prepared in the present work is really the CdSe microcrystals-doped ITO film in which CdSe microcrystals are larger than ones in the film previously prepared.

The wavelength of absorption edge of the composite film is longer than that of pure ITO film as can be seen in Fig. 4, which means that the absorption edge of the composite film corresponds to the absorption edge of the CdSe microcrystal itself. Therefore, it can be said that the absorption edge of the CdSe microcrystal is sited at $\sim$ 420 nm (obtained from α^2 versus photon energy plot [10] as shown in Fig. 8), or at shorter wavelength than that (720 nm) of the bulk CdSe, which is explainable in terms of the small size of the CdSe microcrystal or quantum size effect as in the other microcrystal-doped glass films.

The observed luminescence was red in colour, in accordance with that previously reported [5]. The

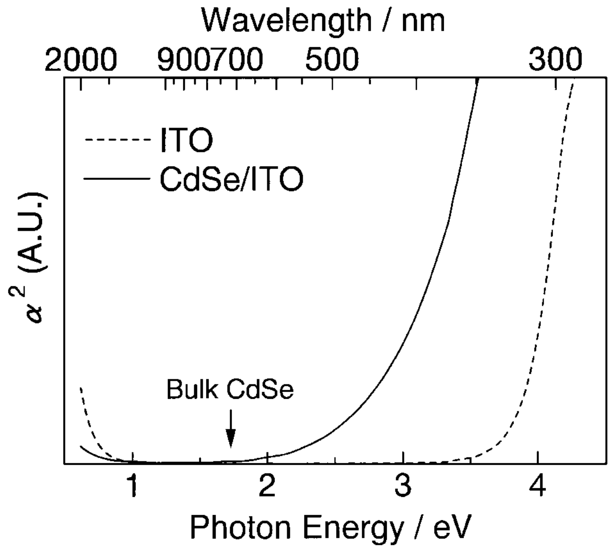

Figure 8 α^2 versus photon energy plots of the CdSe microcrystal-doped ITO film (solid line) and the pure ITO thin film (broken line) calculated using Fig. 4.

spectrum was a combination of visible luminescence (at 710 nm) and near infrared luminescence (at 880 nm and longer wavelength). Unfortunately, comparison of the spectrum with the previous one is not sufficient because the previous one has been limited only to ~ 850 nm or less because of the lower photosensitivity of the detector. However, a faint hump observed around 700 nm in the spectrum shown in Ref. 5 might correspond to the peak appearing at 710 nm in the present work.

For interpreting the luminescence observed in the CdSe microcrystal-doped ITO film, several factors should be taken into consideration. In order to approach one question whether ITO film itself contributes to the luminescence or not, the luminescence spectrum was measured for pure ITO film under the same measurement condition and the application of d.c. voltage of 4 V. However, pure ITO film exhibited no luminescence in the wavelength range from 550 to 950 nm.

A second probable origin of the luminescence may be the thermal effect or black body radiation, since the film sample should be electrically heated during measurements. Actually, the surface temperature of the sample was about 200 °C during the luminescence measurement. Such a thermal effect can be deduced from the luminescence relaxation measured with and/or without HA30 filter. Without filter, whole luminescence took 4 s for the complete relaxation after the applied voltage was removed. The relaxation of the luminescence in the short wavelength range (measured with the filter), in which 710 nm peak is included, was faster than whole luminescence. From these facts, it is considered that the luminescence of longer wavelength than 900 nm may have its origin from the thermal effect or black body radiation, and the luminescence at 710 nm is EL.

The relaxation of EL peaking at 710 nm, however, is not sufficiently fast. If this luminescence has pure EL origin, it is expected to be off as soon as the applied d.c. voltage is turned off; in other words, the relaxation curve measured with the filter should correspond with the decay curve (Fig. 7) of voltage. This still slow relaxation of 710 nm luminescence can be interpreted by considering the overlapping of the tail of the slower relaxation component, or black body radiation occurring in the longer wavelength range.

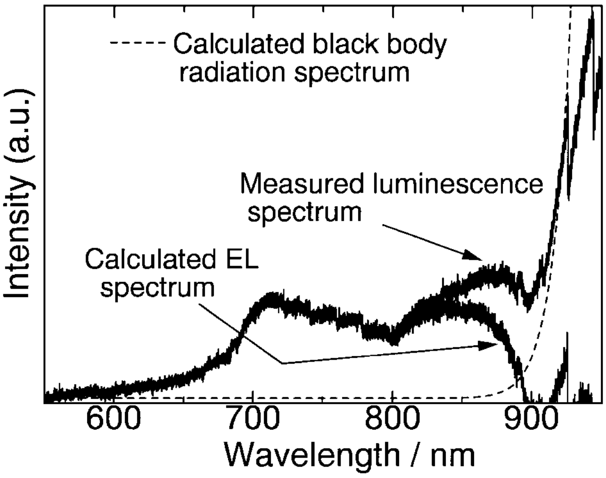

Figure 9 Electroluminescence spectrum subtracted the black body radiation from luminescence spectrum of the film at d.c. 4 V. The black body radiation spectrum at the substrate temperature of 200 °C was calculated by using Planck's law.

The spectrum of the black body radiation at 200 °C, which is the surface temperature of the composite film upon the application of 4 V d.c. voltage, is shown in Fig. 9. From Fig. 9, it is clearly seen that the black body radiation can explain the luminescence at longer than ~ 900 nm.

As to the luminescence peak at ~ 880 nm, it is still difficult to conclude that this luminescence has pure EL origin, as only one filter was used in the present work. However, considering that black body radiation gives rise to a monotonous luminescence profile, as shown in Fig. 9, and the 880 nm-peak grew without changing its position as the applied voltage was increased as well as 710 nm-peak, the 880 nm luminescence peak is also considered to be EL.

Consequently, it is very probable that in the CdSe microcrystal-doped ITO film we have two separated EL peaks at 710 and 880 nm overlapping on the black body radiation, which has not been clearly mentioned in the previous paper [8]. Two luminescence peaks may be interpreted as follows.

In general, the most probable origin of EL is that related to the band gap of semiconductor. The luminescence wavelength for the present composite film is very close to the band gap of bulk CdSe (720 nm). However, in the composite film, absorption edge of CdSe is at ~ 400 nm and far from that of the bulk CdSe caused by the quantum size effect. During the application of voltage, the size of microcrystals might happen to occur because of the increase of the temperature by electric heating. If this would be the case, the luminescence wavelength would be changed to 710 nm, when applied voltage was increased, as the band gap energy changes with the particle size. However, from Fig. 5, the peak position of luminescence is seen not to change when the applied voltage is increased. Further, when the d.c. voltage was applied to the composition film, repeatedly, the peak position of luminescence is not changed. Therefore, it is suggested that the luminescence at 710 nm is not explained in terms of the band gap of CdSe microcrystal. From the above, the peak of 710 nm may be the luminescence associated with the surface defect energy level of semiconductor microcrystals.

Although the particle size of microcrystals in the present film is different from that in the film of the previous report [8], however, the colour of luminescence is same. This fact also suggests that the luminescence does not depend on the particle size of microcrystals.

As to the origin of the peak of 880 nm, the electron transition between the conduction band of CdSe semiconductor and the valence band of ITO matrix could be taken into consideration. If the luminescence of 880 nm is related with such electron transition phenomenon, the peak position of luminescence should be changed for the different applied voltage, because the conduction band of microcrystals would be changed because of the quantum size effect. Therefore, another origin has to be assigned to the peak of 880 nm. Eventually, the electron transition associated with the surface defect of semiconductor microcrystals is also tentatively proposed as the origin of the 800 nm luminescence.

5. Conclusions

CdSe microcrystals doped ITO thin film was successfully obtained by RF-magnetron sputtering method using composite target consisting of a CdSe chip and ITO, and the successful doping was certain from XRD and XPS measurements. From the result of the optical absorption spectra, the blue shift of the absorption edge of the CdSe microcrystals was observed and the quantum size effect was confirmed. The red colour luminescence was observed from the prepared film when d.c. voltage of higher than 3 V was applied. The luminescence spectrum consisted of two peaks at about 710 and 880 nm, and an ascending tail at longer than 900 nm. It was considered that from the luminescence relaxation experiment the luminescence at longer than 900 nm was the thermoluminescence due to black body radiation, and the luminescence at about 710 and 880 nm was electroluminescence. It was also considered that the origin of this luminescence may not be the electron transition associated with the semiconductor of microcrystals themselves because the luminescence wavelength do not depends on the particle size of microcrystals, but the 710 nm and 880 nm luminescence was possibly attributed to the electron transition related to the surface defects of semiconductor microcrystals.

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