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Influence of Ag concentration and post-deposition annealing on $Gd_3Ga_5O_{12}$/Ag thin film electroluminescence ☆

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Abstract

We have investigated the dependence on various Ag concentration for photoluminescence (PL) and electroluminescence (EL) of $Gd_3Ga_5O_{12}$/Ag thin film, respectively. A rapid quenching of PL is observed above 0.2 at.% of Ag concentration due to lattice defects and impurity atoms. However, the optimal concentration of Ag in the EL efficiency is about 1 at.%. This may be attributed to excited state electrons that are not easily trapped by annihilation centers in EL and a 'narrower' forbidden band. The lattice absorption edge is red shifted with increasing Ag concentration. Post-deposition annealing has greatly reduced the lattice imperfections, and improved the PL and EL intensity. The best luminance of the EL devices annealed at 450°C is about 20 cd/m^2 when driven at 5000 Hz. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TFEL; Concentration quenching; Oxide phosphor

1. Introduction

Alternating-current thin film electroluminescence (ACTFEL) has become of great interest since it offers a possible means of achieving high performance in flat panel displays. Thus many studies have been conducted for the purpose of developing multicolor EL devices using various phosphors. Most recently, a number of efficient oxide EL phosphors have been discovered, which demonstrate high brightness and stability [1–4]. For example, TFEL devices using manganese-activated $ZnGa_2O_4$ [1] or $CaO–Ga_2O_3$ [3] phosphor as the emitting layer produce a green emission with a luminescence of 230 cd/m^2 and a yellow emission of 261 cd/m^2, respectively, when driven at 60 Hz. However these oxides provide only high luminescence in green and yellow emission. In order to obtain bright blue emission from TFEL devices using oxide phosphors, which is an important problem for full color EL displays, it is necessary to develop new thin film phosphor materials. Recently, an efficient blue photoluminescence (PL) composite material $Gd_3Ga_5O_{12}/SiO_2$ had been investigated by Wang et al. [5].

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We have investigated a novel blue EL oxide phosphor $Gd_3Ga_5O_{12}$/Ag. The EL spectrum of the device is located at 469 nm. In order to obtain a high blue luminescence of this phosphor, we have investigated the dependence of EL on Ag concentration. A rapid quenching of PL is observed when the Ag concentration is increased above 0.2 at.%. But, in the case of EL the concentration of Ag may be increased up to 1 at.% without quenching. From the absorption spectrum of the thin film with various concentrations of Ag, we find the reason for the difference of EL and PL dependence on Ag concentration. Finally, we also investigated the post-deposition annealing of the phosphor. The post-deposition annealing has greatly reduced the lattice defects of lattice, and enhanced the PL and EL efficiency.

2. Experiments

$Gd_3Ga_5O_{12}$/Ag was prepared by mixing three components: Gd_2O_3 (purity 99.99%), Ga_2O_3 (99.99%) and $AgNO_3$ (99.9%). Their weights were chosen in order to get a stoichiometric compound with various Ag concentrations (0.1,0.2,0.5,1,3,5 at.%). The mixture of them was pressed into pellets, and then sintered [6]. The structure of our devices was ITO/SiO/SiO_2/phosphor/SiO_2/SiO/Al (Fig. 1). The thickness of SiO, SiO_2, and $Gd_3Ga_5O_{12}$/Ag were 40,

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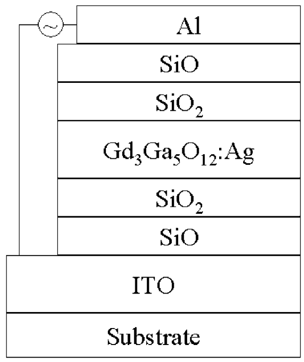

Fig. 1. Structure of the devices.

25, and 150 nm, respectively. They were deposited on glass covered with ITO by electron beam evaporation at nominal deposition rate 0.3, 0.13, and 0.04 nm/s, respectively. In the process the substrate temperature was kept at 275°C. The samples were annealed in air at 350, and 450°C for 3 h.

The PL and EL for the phosphor were measured by means of HITACHI-4010 Fluorescence Spectrophotometer. Optical absorption spectra were measured with a SHMADIU UV-31010PC UV–Vis–NIR Scanning Spectrophotometer. The phosphor film for absorption measurement was deposited on quartz substrate, with the same thickness of 15 nm. In the EL measurements, the devices were excited by an alternating-current sinusoidal voltage with frequency of 5000 Hz.

3. Results and discussion

We have investigated the crystallinity of the phosphor powder and thin film, PL and EL spectra previously (Fig. 2). The PL spectrum has two peaks located at 397 and 469 nm. However, the EL has only one peak at 469 nm in the devices of this structure. The samples were excited by monochromatic 330 nm light from a Xe lamp. This corresponds to the excitation of host lattice. When the sample is irradiated with the light of a 330 nm wavelength, the excitation of Ag^+ ion is via resonant energy transfer process where the energy released from the recombination of an electron–hole pair is transferred to the Ag^+ ion. Fig. 3 shows the dependence of PL and EL on Ag concentration. The PL intensity shows a maximum value at 0.2 at.%. However, the concentration for optimal EL efficiency is about 1 at.%. The strong concentration quenching in PL can be interpreted as follows. When an excess of Ag is forcibly doped into the $Gd_3Ga_5O_{12}$ film by thermal nonequilibrium manner such as electron beam evaporation, lattice defects and impurity atoms are naturally introduced to compensate the charge imbalance between Ag^+ and Gd^{3+} ions. Consequently, various kinds of complexes are formed in the $Gd_3Ga_5O_{12}$, and thus excitons are subject to nonradiative annihilation because of the poor crystal quality induced by the high density of imperfection. However, the concentration quenching in EL is thought to be negligible compared to radiative emission, when the Ag concentration is lower than 1 at.%.

Fig. 4 shows the absorption spectra of $Gd_3Ga_5O_{12}$ thin film without and with various Ag concentrations. It can be seen that the lattice absorption edge is red shifted with increasing Ag concentration, the shift is about 12 nm from undoped to doped with 3 at.% Ag. This red shift may be induced from the shallow impurity energy level in the band gap. We have changed the insulator and activated centers for the $Gd_3Ga_5O_{12}$ TFEL devices, we can also obtain the EL emission at 330 nm (described elsewhere), which coincides with interband emission. From this we can know that the interband excitation is also a main part of excitation in the

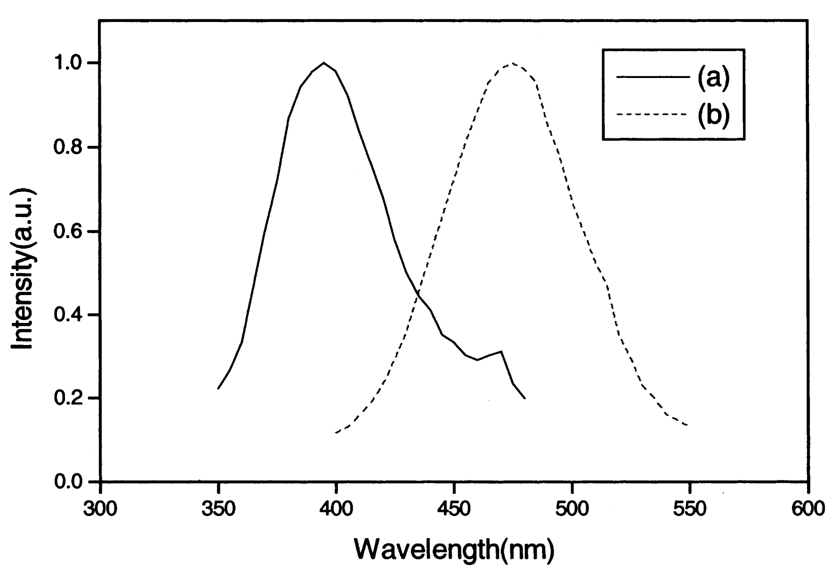

Fig. 2. PL (a, exited by 330 nm) and EL (b) spectra of the devices.

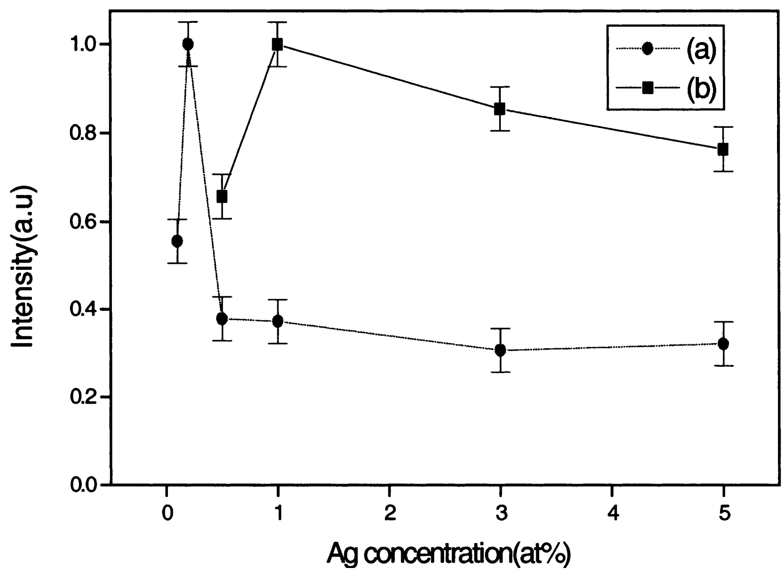

Fig. 3. Dependence of PL (a) and EL (b) intensity on the Ag concentration for $Gd_3Ga_5O_{12}$ thin film electroluminescence. Wavelength of the exciting light is 330 nm.

$Gd_3Ga_5O_{12}$/Ag TFEL. The absorption edge red shift has also improved the excitation efficiency by electrical field, because a 'narrower' band for interband excitation may reduce the excitation energy of electron collision. This may be another explanation for the concentration to optimize the EL efficiency of 1 at.%, which is five times as high as that of PL.

The relative changes of PL intensity with the temperature of post-deposition annealing are shown in Fig. 5. The excitation of the film is at 330 nm. Ag concentrations in all samples are almost the same at 1 at.%. The PL intensity after annealing at 450°C is seven times as large as that of an unannealed sample. The facts clearly indicate that the efficiency of energy transfer from electron–hole pairs to Ag^+ ions is undoubtedly improved by high temperature annealing. It is well known that annealing the $Gd_3Ga_5O_{12}$ film at 450°C tends to promote the relaxation of lattice strain and the reduction of lattice imperfections. Improvement of crystal quality may play a significant role in enhancing the PL efficiency.

The effect of post-deposition annealing on luminescence of the devices can also be seen from the intensity of EL. We cannot observe the EL emission on an unannealed film due to the breakdown of the device. The best luminescence of

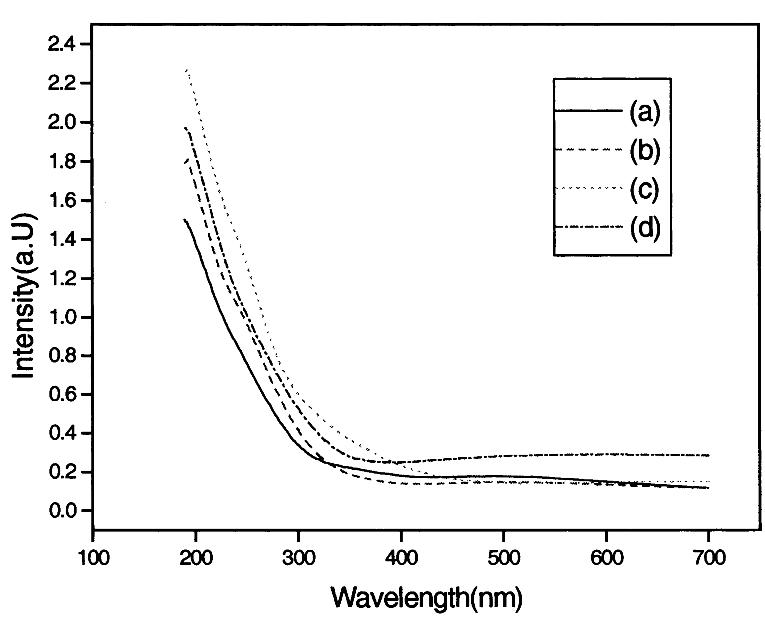

Fig. 4. Absorption of $Gd_3Ga_5O_{12}$ thin film without (a) and with various Ag concentration, 0.5 at.% (b), 1 at.% (c), 3 at.% (d).

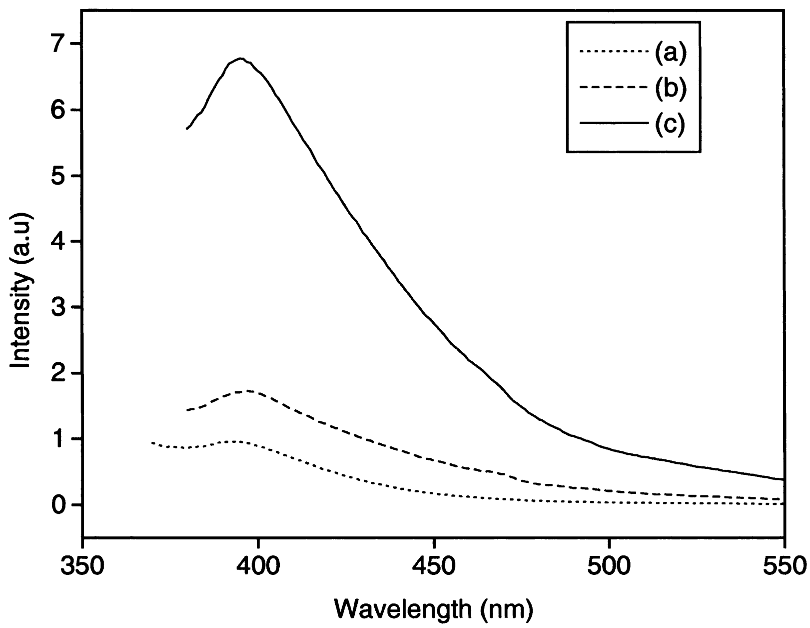

Fig. 5. Dependence of PL intensity on $Gd_3Ga_5O_{12}$:Ag thin film annealed at various temperatures: as-deposition (a), 350°C (b), 450°C (c).

the EL devices annealed at 450°C is about 20 cd/m^2 when driven at 5000 Hz.

In this paper, the discussion on the dependence of Ag concentration on $Gd_3Ga_5O_{12}$/Ag TFEL has been primarily devoted to a concentration quenching of PL and EL. A rapid quenching of PL is observed above 0.2 at.% of Ag concentration due to lattice defects and impurity atoms. The concentration to optimize the EL efficiency about 1 at.% resulted from higher collision efficiency for a narrower band. Post-deposition annealing has greatly reduced the lattice imperfections, improved the PL and EL intensity. Further investigation is required to determine the main reason for low luminescence factors such as the thickness of insulator, luminescent efficiency, etc.

4. Conclusions

In conclusion, we have investigated the dependence on various Ag concentrations for PL and EL, respectively. A rapid quenching of PL is observed above 0.2 at.% of Ag concentration because of lattice defects and impurity atoms. The concentration to optimize the EL efficiency at about 1 at.% is explained by higher collision efficiency. This may be due to the lattice absorption edge being red shifted with increasing Ag concentration. Post-deposition annealing has greatly reduced the lattice imperfections, improved the PL and EL intensity.

References

[1] T. Minami, T. Maeno, Y. Kuroi, S. Takata, Jpn. J. Appl. Phys. 34 ((Part 2, 6A)) (1995) L684–L687.

[2] T. Xiao, A.H. Kitai, G. liu, A. Nakua, J. Barbier, Appl. Phys. Lett. 72 (25) (1998) 3356–3358.

[3] T. Minami, H. Yamada, Y. Kubota, T. Miyata, Jpn. J. Appl. Phys. 36 ((Part 2, 9A/B)) (1997) L1191–L1194.

[4] S.H.M. Poort, D. Cetin, A. Meijerink, G. Blasse, J. Electrochem. Soc. 144 (6) (1997) 2179–2183.

[5] J. Wang, Y. Yoo, C. Gao, I. Takeuchi, X. Sun, H. Chang, X.-D. Xiang, P.G. Schultz, Science 279 (1998) 1712–1714.

[6] X. Xu, Z. Xu, Y. Hou, X. Wang, X. Chen, X. Xu, Chin. Phys. Lett. 16 (5) (1999) 387–388.