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Thin Solid Films 306 (1997) 160–162

thin solid films

Preparation of $CaGa_2S_4$:Ce TFEL devices with inter-layer reaction [1]

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Received 17 October 1996; accepted 13 March 1997

Abstract

Ce^{3+}-doped alkaline earth thiogallates with blue emission have been intensively investigated to fabricate full-color thin film electroluminescence (TFEL) devices, with sputtering, atom layer epitaxy (ALE) and molecular beam epitaxy (MBE) being the methods used. In this paper, a new way of preparing $CaGa_2S_4$:Ce TFEL devices, based on inter-layer reaction is first reported. CaS:Ce and Ga_2S_3 were deposited by electron beam evaporation, layer by layer, and $CaGa_2S_4$:Ce thin film was formed by post processing. The results of X-ray diffraction, scanning transmission electron microscopy (STEM) microphotographs and energy dispersive X-ray spectroscopy (EDX) show that $CaGa_2S_4$:Ce thin film with good crystallinity and stoichiometry were obtained. Photoluminescence (PL) and electroluminescence (EL) of these devices were investigated. © 1997 Elsevier Science S.A.

Keywords: Annealing; Crystallization; Evaporation; X-ray diffraction

1. Introduction

Thin film electroluminescence (TFEL) is an important technology for flat plant display. Up to now, monochromatic TFEL products have been sold in the display market. In recent years, interests are focused on multi-color and full-color TFEL devices.

$M$$Ga_2S_4$:Ce ($M$ = Ca, Sr, Ba) is a family of phosphors which have a wide band gap, strong blue emission and good color purity. There are hopeful candidates for obtaining bright blue TFEL. Sputtering [1,2], atom layer epitaxy (ALE) [3] and molecular beam epitaxy (MBE) [4] are usually used to prepare these devices. In this paper, the inter-layer reaction method is first reported. An insulator layer with high dielectric constant, such as $BaTiO_3$ and $BaTa_2O_6$ [1–4], is used in conventional sandwich structure because of the high dielectric constant of $M$$Ga_2S_4$:Ce, but in our layered structure [5], SiO/SiO_2/$CaGa_2S_4$:Ce/SiO_2/SiO was prepared.

2. Experimental

CaS and Ga_2S_3 were synthesized by sintering $CaCO_3$ and Ga_2O_3 in H_2S atmosphere for 1.5 h at 1150°C and 1050°C, respectively. Ga_2S_3 and the mixture of CaS and CeF_3 were pressed into pieces, then sintered in H_2S atmosphere at 1050°C for 1 h. The concentration of Ce^{3+} is 5 mol%. SiO and SiO_2 were deposited unto the quartz substrate with ITO by means of electron beam (EB) evaporation. Then very thin CaS:Ce and Ga_2S_3 layers were evaporated with the same way alternately. Sulfur was co-evaporated during the preparation of the CaS:Ce and Ga_2S_3 thin films. After 20 periods, the samples were annealed in H_2S atmosphere at 550°C for 30 min after which the second SiO_2 and SiO layers were evaporated by EB evaporation. The thickness of SiO and SiO_2 are 36 nm and 64 nm, respectively. The samples were annealed in Ar

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[1] Supported by National Nature Science Foundation of China.

PII S0040-6090(97)00153-3

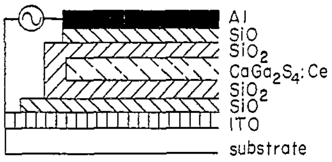

Fig. 1. Structure of device.

atmosphere for 20 min at 600°C, 700°C and 800°C, respectively. Al electrodes were deposited by thermal evaporation (Fig. 1).

The concentration of each element of the active layer was measured by energy dispersive X-ray spectroscopy (EDX) with a JEM-2000FX scanning transmission electron microscopy (STEM). The crystallinity was analyzed by X-ray diffraction (XRD) patterns and microphotographs. The spectra of photoluminescence (PL) and electroluminescence (EL) for the thin films were measured using HITACHI F-4010 fluoresce spectrophotometer.

3. Results and discussion

The concentration of each element of the active layer, namely Ca, Ga, S and Ce, were calculated according to the EDX which shows that the thickness of CaS:Ce and Ga_2S_3 were evaporated according to the stoichiometry of $CaGa_2S_4$, such as 5.36 nm CaS:Ce and 10 nm Ga_2S_3 for a period. The concentration of each element are Ca: 10.62 mol%, Ga: 40.61 mol%, S: 48.52 mol% and Ce: 0.24 mol%. The mole ratio of these four elements is 0.52:2:2.39:0.012. Obviously, the concentration of Ca, S and Ce in the active layer is lower than the stoichiometry because of their different saturation vapor pressures. When the proportion of CaS:Ce to Ga_2S_3 was changed to 10 nm:10 nm, the concentration of Ca, S and Ce increased. The concentration of each element became Ca: 13.57 mol%, Ga: 28.57 mol%, S: 54.26 mol% and Ce: 0.46 mol%. The mole ratio 0.95:2:3.8:0.032 is very close to the stoichiometry of $CaGa_2S_4$:Ce.

The structure and form of the active layer were analyzed with XRD and STEM. Fig. 2 shows the XRD patterns for the samples annealed at different temperature. No diffraction peak was observed for the sample annealed at 550°C. The intensity of the XRD peaks increased with the temperature for the samples annealed at above 600°C. The positions of the peaks are identical with the XRD cards. These results indicated that the chemical composition of the active layer is $CaGa_2S_4$:Ce and the crystallinity improved with increasing temperature. The XRD patterns of the films were simpler than those of $CaGa_2S_4$:Ce powder. There are 6 peaks for the powder and 3 for the thin films in the range $15° < 2\theta < 45°$. These results shown that $CaGa_2S_4$:Ce thin film grew along (400,040), (422) and (062) orientation.

The microphotographs show the same results. The photo is obscure for the sample annealed at 550°C and the grains distribute regularly for that annealed at above 600°C. The former was amorphous and the crystallinity improved with annealing temperature for the latter.

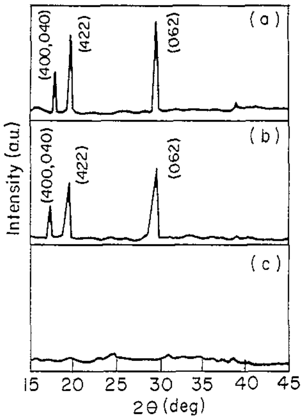

Fig. 2. X-ray diffraction patterns of $CaGa_2S_4$:Ce TFEL devices annealed at (a) 800°C (b) 600°C and (c) 550°C.

In the PL, two excitation peaks (Fig. 3a), at 340 nm and 418 nm, were observed for the sample annealed at 800°C. The intensity of 418 nm peak is much higher than that at 340 nm. The peak at 340 nm originates from the inter-band absorption of $CaGa_2S_4$ and the 418 nm peak originates from the transition from the ground state to excitation state of Ce^{3+}. The latter excited the luminescence center much more efficiently than the former. The PL (Fig. 3b) of the film excited by 420 nm showed two broad peaks located at 469 nm and 520 nm, originating from the $^2D(5d) \rightarrow ^2F_{5/2}(4f)$ and $^2D(5d) \rightarrow ^2F_{7/2}(4f)$ transitions, respectively, but no PL and EL were observed for the sample annealing at 550°C.

The EL spectrum (Fig. 3c) was measured. This is shifted to short wavelength relative to the PL a little. In our layered structure, the dielectric constants of SiO and SiO_2 are less than those of $CaGa_2S_4$, and the hot electrons are preheated [6] and accelerated [5,7] before they enter the active layer, so the electrons can attain a higher energy than those in a conventional structure. Although the electric field in the SiO_2 layer is higher than that in $CaGa_2S_4$:Ce, EL has been observed. The band offset

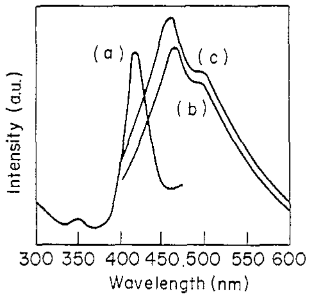

Fig. 3. PL and EL of $CaGa_2S_4$:Ce TFEL device. (a) excitation spectrum (b) PL and (c) EL.

between the SiO_2 and $CaGa_2S_4$:Ce layers and the excitation mechanism are to be investigated.

4. Conclusion

CaS:Ce and Ga_2S_3 were deposited layer by layer by EB evaporation. Sulfur was compensated by S co-evaporation and annealing in H_2S atmosphere. $CaGa_2S_4$:Ce thin film was formed by inter-layer reaction between CaS:Ce and Ga_2S_3 layers during the aforementioned process. EL was observed in the layered structure. The influences of annealing on the stoichiomity, crystallinity and luminescent characteristics were investigated.

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