OPTICAL PROPERTIES OF Ce-DOPED $CaGa_2S_4$ AND $SrGa_2S_4$ FILMS PREPARED BY FLASH EVAPORATION METHOD

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Ce-doped $CaGa_2S_4$ and $SrGa_2S_4$ thin films were prepared for the first time by the flash evaporation method. The films were characterized before and after annealing in H_2S(10%)+Ar gas stream by measuring photoluminescence and absorption spectra, X-ray diffraction and electron probe micro analyses (EPMA). X-ray diffraction curves and absorption spectra before annealing show amorphous behaviour, whereas the annealing leads to a significant crystallization and improves the stoichiometry of the films. Based on the performance data obtained from dispersive type EL cells using $CaGa_2S_4$:Eu powder together with photoluminescence property comparison between $CaGa_2S_4$:Eu and $CaGa_2S_4$:Ce powders, the annealed films prepared by flash evaporation can be considered to become one of the candidates for TFEL flat panel devices.

Keywords: $CaGa_2S_4$, $SrGa_2S_4$, Ce impurity, photoluminescence, thin film, electroluminescence

1. Introduction

The cerium-activated calcium and strontium thiogallate ($CaGa_2S_4$:Ce, $SrGa_2S_4$:Ce) thin films are regarded as one of the most promising pure blue phosphor materials and successfully used as thin film electroluminescent (TFEL) flat panel devices [1]. There are various techniques to obtain the $CaGa_2S_4$ and $SrGa_2S_4$ thin films. Molecular Beam Epitaxy (MBE) [2], sputtering [1], deposition from binary vapours (DVB) [3], etc. are usually used for preparing of TFEL devices.

In the present paper, optical characterizations of Ce^{3+} activated $CaGa_2S_4$ and $SrGa_2S_4$ thin films prepared by the so-called flash evaporation method are given for the first time. This method is simple and inexpensive as compared with the above mentioned methods. Feasibility of TFEL device construction from $CaGa_2S_4$:Ce^{3+} and $SrGa_2S_4$: Ce^{3+} thin films is discussed based on operational data of dispersive type EL cells made from $CaGa_2S_4$:Eu powder.

2. Experimental

$CaGa_2S_4$:Ce and $SrGa_2S_4$:Ce thin films were prepared by the flash evaporation method. Prior to thin film preparation, polycrystalline powders of $CaGa_2S_4$:Ce (3 at.%) and $SrGa_2S_4$:Ce (3 at.%) were prepared by solid-state reaction of a mixture of high purity CaS, Ga_2S_3, Ce_2S_3 and SrS, Ga_2S_3, Ce_2S_3 powders, respectively, at 900°C for 24 hours under H_2S(10%)+Ar stream. The obtained powders were ground and discretely evaporated onto a

quartz substrate from a tantalum boat by means of a special feeding appliance. The temperature of the boat was kept approximately 1500 °C. The substrate was heated by radiation from the boat. The temperature of the substrate depended on the distance from the boat and could be changed in the range of 200 - 600 °C. The thickness of the obtained film depended on the number of discrete evaporation and varied within 100 - 2000 nm. An annealing process of the film was performed under H_2S(10%)+Ar gas stream at 750 °C for 1 hour.

X-ray diffraction curves of the samples were measured by a diffractometer (Rigaku, RAD III) using the Cu-Kα radiation (1.54065 Å). The composition analyses of the samples were accomplished by an electron probe micro-analyzer with an energy-dispersive X-ray (EDX) mode (JEOL, 3203-JXA N2426) using a 10 keV electron beam.

Measurements of photoluminescence and absorption spectra were performed at room temperature using a 441.6 nm He-Cd laser (Omnichrome, 4056-M-A10) for the former and an Xe arc lamp for the latter, respectively. The luminescence from the samples was dispersed through a grating monochromator (Nalumi, RM-23) and was detected by a photomultiplier (Hamamatsu, R943-02) with a photoncounter (Hamamatsu, C767). The film thickness was measured by the interference method using a microscope (Nikon, Optiphot). Time decay of the photoluminescence were measured at room temperature. The excitation source was a dye laser (Lambda Physik, FL 3002, stilbene 420, 4250 Å) with 15 ns pulse duration pumped by an Xe-Cl laser (Lambda Physik, LEXTRA 200) operating at 10 Hz. Temporal variation of the output from a photomultiplier (Toshiba, PM55) in conjunction with a monochromator (Instruments SA, HR-320) was displayed on a digital oscilloscope (Sony Tektronix, TDS 380P).

Dispersive type EL cells were prepared by spreading a mixture of $CaGa_2S_4$:Eu (1 at.%) powder and glue on a SnO_2/glass substrate. Aluminium was evaporated on the mixture to make another electrode. The EL cells were driven by a function generator (Hewlett Packard, 8166A) coupled with an amplifier (Aiwa, MX-R). Luminance of the EL cells was measured using a luminance meter (Minolta, T-1).

3. Results and Discussion

X-ray diffraction patterns for $CaGa_2S_4$:Ce and $SrGa_2S_4$:Ce powder samples confirmed the formation of polycrystalline structure, which possess the orthorhombic modification. The obtained powders can be practically considered as the mono-phase compounds, though a few weak lines are seen indicating the presence of a little amount of Ga_2S_3, CaS, SrS phases.

The photoluminescence spectra of $CaGa_2S_4$:Ce and $SrGa_2S_4$:Ce powder samples showed the characteristic emissions consisting of double bands with peaks at 470 nm and 515 nm for the former, and at 450 nm and 495 nm for the latter, respectively. The emission is considered to arise from the parity-allowed transition between the 5d and 4f states of the Ce^{3+} ion. The energy difference between two emission peaks in both compounds is about 0.27 eV. This value is in good agreement with the value of 0.28 eV, as the difference reported for two

lowest states $^2F_{5/2}$ and $^2F_{7/2}$ of single 4f electron configuration of trivalent cerium [3]. For $CaGa_2S_4$:Ce and $SrGa_2S_4$:Ce, the decay time constants were found to be 24.2 and 24.3 ns, respectively. The values are in good agreement with the value of 24.5 ns reported earlier [4,5].

X-ray studies showed that the $CaGa_2S_4$:Ce film immediately after deposition exhibited amorphous behaviour in the whole substrate temperature range studied. Fig. 1(a) shows an X-ray diffraction curve of the film deposited at 490 °C. For $SrGa_2S_4$:Ce the situation was similar. EPMA results show some sulphur deficiency in the films. The thermal treatment of the films in H_2S(10%)+Ar stream leads to significant crystallization of amorphous films. Figure 1(b) shows the X-ray diffraction curve for the annealed $CaGa_2S_4$:Ce thin film. EPMA measurements of $CaGa_2S_4$:Ce films after annealing indicate nearly the stoichiometric composition. In the case of $SrGa_2S_4$:Ce films the ratio of Ga to S was found to be close to 1:2, though one cannot determine the composition of Sr due to strong overlapping of Sr signal and Si signal from the quartz substrate. Thus in both films the annealing in H_2S atmosphere is considered to recover the sulphur deficiency.

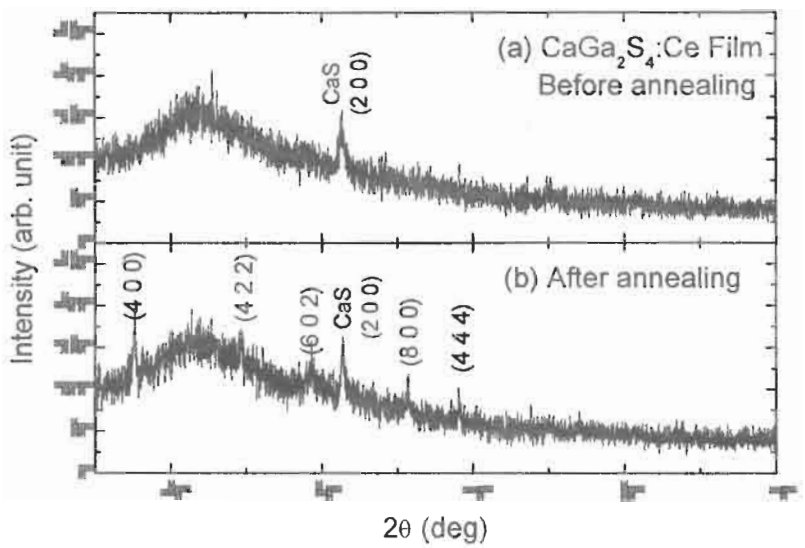

Fig. 1 X-ray diffraction curves for a $CaGa_2S_4$:Ce film before (a) and after (b) annealing under H_2S(10%) + Ar gas stream at 750□ for 1 hour.

Figure 2 shows the optical absorption spectra of $CaGa_2S_4$:Ce film before and after annealing. The shapes of the spectrum before annealing is quite similar to the imaginary part of the reported dielectric function spectrum of amorphous $CaGa_2S_4$ obtained by rapid-cooling of molten $CaGa_2S_4$ [6]. The energy difference between the absorption edges of amorphous and crystalline phases in Ref. [6] was reported to be about 0.3 eV. The annealing of the film seems to produce this corresponding shift of the edge towards higher energies as seen in Fig. 2. The same situation takes place in $SrGa_2S_4$:Ce films. Optical absorption edges of these films after annealing were found to be at 4.15 eV and 4.35 eV, corresponding to the reported

band gap energies [6, 7] of crystalline $CaGa_2S_4$ and $SrGa_2S_4$ compounds, respectively. The amorphous phase of the flash-evaporated films could be related with the rapid cooling process of the substance from the evaporating temperature of 1500 °C to the substrate temperatures of 200 - 600 °C. During this process a loss of sulphur could occur, causing the deficiency of S atoms in the films.

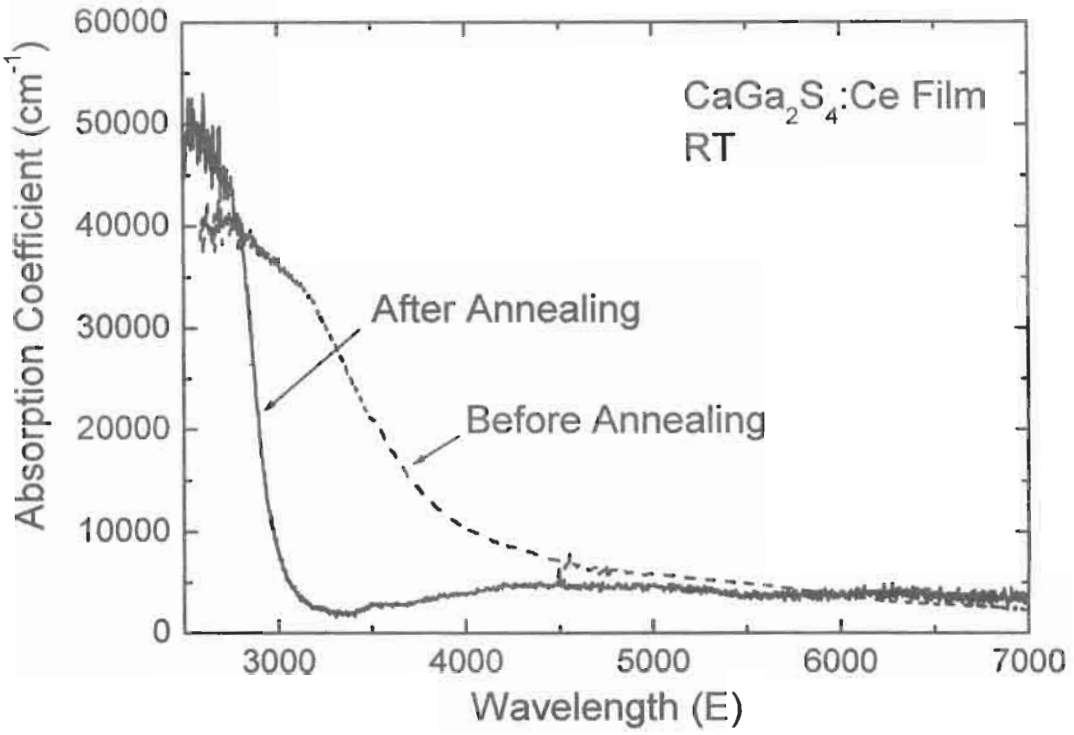

Fig. 2 Optical absorption spectra of a $CaGa_2S_4$:Ce film before (broken line) and after (solid line) annealing under H_2S(10%) + Ar gas stream at 750□ for 1 hour. The thickness of the film was 900 nm.

Figure 3 shows the photoluminescence spectra of the $CaGa_2S_4$:Ce film before and after annealing. Figure 4 shows a photoluminescence spectrum of an annealed $SrGa_2S_4$:Ce film. $CaGa_2S_4$:Ce and $SrGa_2S_4$:Ce films before annealing exhibited the weak emission consisting two-emission bands at the same wavelength regions as the corresponding powder samples. However, the intensities of these emissions decreased with time and disappeared within a few days. The characteristic double-band emissions seen just after the deposition could be attributable to the short-range interaction of Ce^{3+} ions with the nearest-neighbouring sulphur atoms, constituting the circumstance similar to the crystals. The degradation possibly may be due to the diffusion of either Ce^{3+} ions from active sites or S atoms with time in amorphous phase.

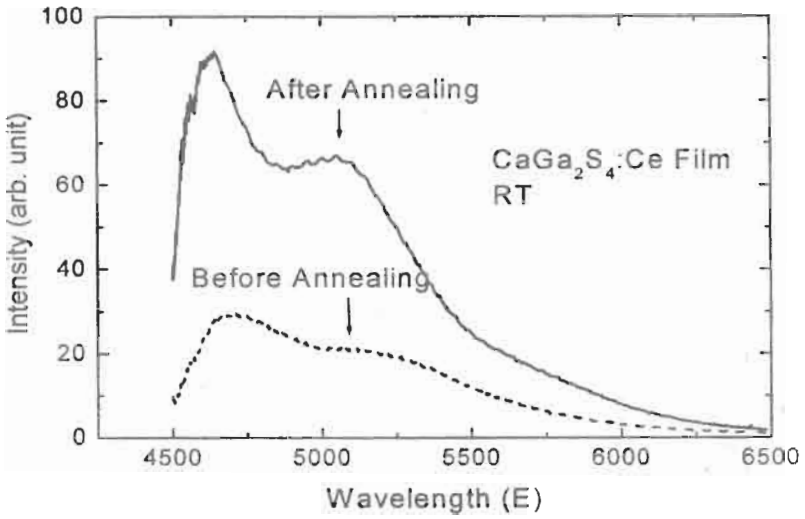

Fig. 3 Photoluminescence spectra of a $CaGa_2S_4$:Ce film before (broken line) and after (solid line) annealing under H_2S(10%) + Ar gas stream at 750°C for 1 hour.

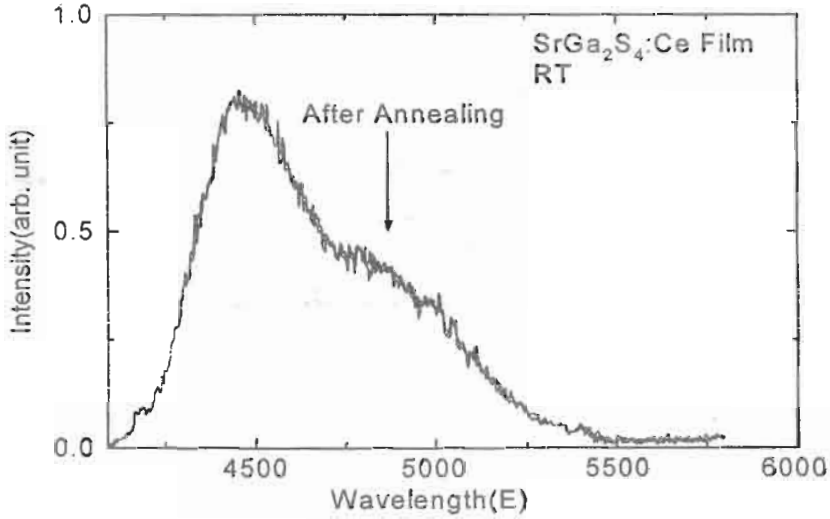

Fig. 4 Photoluminescence spectra of a $SrGa_2S_4$:Ce film annealed under H_2S(10%) + Ar gas stream at 750°C for 1 hour.

After annealing under H_2S(10%)+Ar atmosphere the emission show no degradation and the intensity becomes much higher. Luminescence decay time constants of the annealed films were found to be close to the values for powder samples (for example, in case of $SrGa_2S_4$:Ce film 24 ns).

Dispersive type EL cells using $CaGa_2S_4$:Eu powder give luminance of about 12 cd/m^2 at 500 Hz with operating voltage of 250 V. Usually film type cells have advantages in operating characteristics over dispersive type cells. According to Bénalloul *et al.*, the $SrGa_2S_4$:Eu (2 at.%) TFEL cell prepared by the sputtering method showed higher luminance by about 20x in comparison with the above value at nearly the same operating condition [8].

Since the observed decay time constants of our annealed films are close to the value reported [4] for powder samples with 1 at. % Ce concentration, the emission in our case can be considered not to be affected seriously by non-radiative transition. Photoluminescence quantum efficiencies as high as 73 % [9] and 30 % [10] were observed for $CaGa_2S_4$:Ce (0.8 at.%) and for $CaGa_2S_4$:Eu (1 at.%), respectively. Since the excitation mechanism is different for photoluminescence and TFEL cells, prediction of performance capability for the $CaGa_2S_4$:Ce TEFL cells is difficult. However, if we consider simply both differences of the quantum efficiency and the spectral luminous efficacy between the Eu and Ce emissions, the luminance of thin film Ce EL cells, if constructed, would be about one half of the Eu EL cells.

The conventional conductive layers such as ITO and SnO_2 on glass substrates are not stable at the annealing temperatures of the present films (700 - 750 °C). The utilization of more stable layers or the reduction of annealing temperature is necessary for making TFEL cells using the flash evaporation method. Recently, $CaGa_2S_4$:Ce TFEL devices were reported to be obtained from electron beam evaporated films with annealing in H_2S stream at 600°C [11]. For our case of the flash evaporation, the annealing temperature could be reduced with longer annealing time.

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PARTLAYIŞ BUXARLANMASI ÜSULU VASİTƏSİLƏ HAZIRLANMIŞ Ce AŞQARLI $CaGa_2S_4$ VƏ $SrGa_2S_4$ PLYONKALARININ OPTİK XÜSUSİYÜYƏTLƏRİ

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İlk dəfə olaraq ce aşqarlı $CaGa_2S_4$ və $SrGa_2S_4$ plyonkaları partlayış buxarlanması üsulu ilə hazırlanmışdır. Hazırlanmış nümunələrin fotolyuminesensiya, udullma spektrləri, rentgen difraksiyası və ERMA tədqiqatları, nümunələr 10%-li H_2S+Ar mühitində qızdırılmaqdan əvvəl və sonra yerinə yetirinə yetirilmişdir. Rentgen şualarının difraksiyası və udulma əyrilərindən məlum olur ki, qızdırılmadan əvvəl materiallar amorf xarakterli olduğu halda, qızdırıldıqdan sonra materiallarda kifayət qədər kristallaşma müşahidə olunur və onların stexnometriyası yaxşılaşır. Tədqiqatların nəticələri göstərir ki, hazırlanmış materiallar nazik təbəqəli elektrolyuminesensiya panellərinin hazırlanmasında müvəffəqiyyətlə istifadə oluna bilər.

ОПТИЧЕСКИЕ СВОЙСТВА Ce-ЛЕГИРОВАННЫХ $CaGa_2S_4$ И $SrGa_2S_4$ ПЛЕНОК, ПОЛУЧЕННЫХ МЕТОДОМ ВЗРЫВНОГО ИСПАРЕНИЯ

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Пленки $CaGa_2S_4$ и $SrGa_2S_4$, легированные Ce, впервые получены методом взрывного испарения. Пленки были исследованы до и после отжига в потоке 10% H_2S+Ar путем измерений спектров фотолюминесценции, поглощения, рентгеновской дифракции и ЕРМА. Кривые рентгеновской дифракции и поглощения указывают на аморфный характер пленок до отжига , в то время как, после отжига наблюдается значительная кристаллизация и улучшение стехиометрии полученных пленок. Результаты исследований показывают, что полученные пленки могут быть успешно использованы в создании тонкопленочных электролюминесцентных панелей.