EFFECT OF THERMAL ANNEALING ON STRUCTURAL PROPERTIES OF $SrGa_2S_4$:Ce THIN FILMS PREPARED BY FLASH EVAPORATION

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In the present report, the preparation technology and structural characterization of Ce^{3+} activated $SrGa_2S_4$ thin films are given. $SrGa_2S_4$:Ce thin films are prepared by so called flash evaporation which is simple and inexpensive method for thin film deposition.

X-ray diffraction shows that the "as deposited" films exhibit amorphous behavior, but after annealing in H_2S stream, the polycrystalline one. EPMA results indicate nearly stoichiometric composition of the thin films.

1. INTRODUCTION

Electroluminescent (EL) flat panel devices are regarded as a leading candidate for use as the high-resolution multimedia displays of the future.

The biggest problem with the EL device is their inability to emit pure blue emission with high brightness and stability, although performance for red and green luminescence is already sufficient for practical use. Cerium-activated alkaline thiogallate phosphors have been extensively investigated for use as pure blue EL materials and successfully used as thin film electroluminescent flat panel devices (TFEL) [1-6]. In the thiogallate family, the cerium-activated strontium thiogallate ($SrGa_2S_4$:Ce) thin film is regarded as one of the most promising blue phosphor materials [4].

There are various techniques to obtain the $SrGa_2S_4$ thin films, for example MBE (Molecular Beam Epitaxy) method [5], DBV (Deposition from Binary Vapors) method [7], RF sputtering method [8], MSD (Multi Source Deposition) method [9] or, two electron beam evaporation [10].

In present work the Ce-doped $SrGa_2S_4$ thin films were prepared by so called flash evaporation method. The main distinctions of this method from above mentioned methods are simplicity and cheapness of preparation technology.

X-ray diffraction, electron probe microscopy analysis (EPMA) measurements were carried out for the films obtained by flash evaporation method before and after annealing process.

2. EXPERIMENTAL PART

$SrGa_2S_4$:Ce thin films were prepared by the flash evaporation method. $SrGa_2S_4$:Ce polycrystalline powders, which synthesized by solid state reaction, were ground and discretely evaporated onto a quartz substrate. The evaporation process was done at the vacuum level $1 \cdot 10^{-5}$ torr. The temperature of the tantalum boat was kept approximately 1500°C. The quartz substrate was heated by radiation from the boat. Its temperature depended on the distance from the boat and could be changed in the range of 200-500°C. In this research, at the distance 2 cm, the temperature of substrate was about 400°C.

An annealing process for the thin films was carried out in (10% H_2S+90% Ar) gas stream (50 ccm) at 750°C for 1 hour.

X-Ray diffraction (XRD) of the deposited films were measured by Rigaku RAD III analyzer using Cu-Kα radiation ($\lambda = 1.54056 Å$) as the excitation X-ray source. Ni filter was put in front of receiving slit in order to cut Cu-Kβ radiation. The measurement conditions were: voltage 50.0 kV, electric current 300.0 mA, receiving slit 3.00 mm, divergence slit 1.0°, scan range 15.0°- 60.0°, sampling angle 0.010° and scan speed 4.0°/min.

The composition analysis of the powder was accomplished with an energy dispersive X-ray microanalyzer (JEOL: 3203-JXA Serial Num N2426).

Decay time of the photoluminescence was measured at room temperature. The excitation source was a dye laser (Lambda Physik, FL 3002, Stilbene 420; wavelength 425 nm and pulse 0.5 mJ) with 15 ns pulse duration pumped by an Xe-Cl excimer laser (Lambda Physik, LEXTRA 200) operating at 10 Hz. Temporal variation of the output from a photomultiplier (Toshiba, PM55 in conjunction with monochromator (Instruments SA, HR-320) was displayed on a digital oscilloscope (Sony Tektronix, TDS 380 P).

3. RESULTS AND DISCUSSION

The X-ray diffraction curve for Ce doped $SrGa_2S_4$ thin film before annealing process is shown at fig. 1a. As seen from the fig. 1a, the film doesn't show any reflection lines and exhibits amorphous behavior. The temperature and duration of deposition process in flash evaporation method seems to be not enough for the crystallization of deposited film. Therefore the annealing of obtained films is necessary.

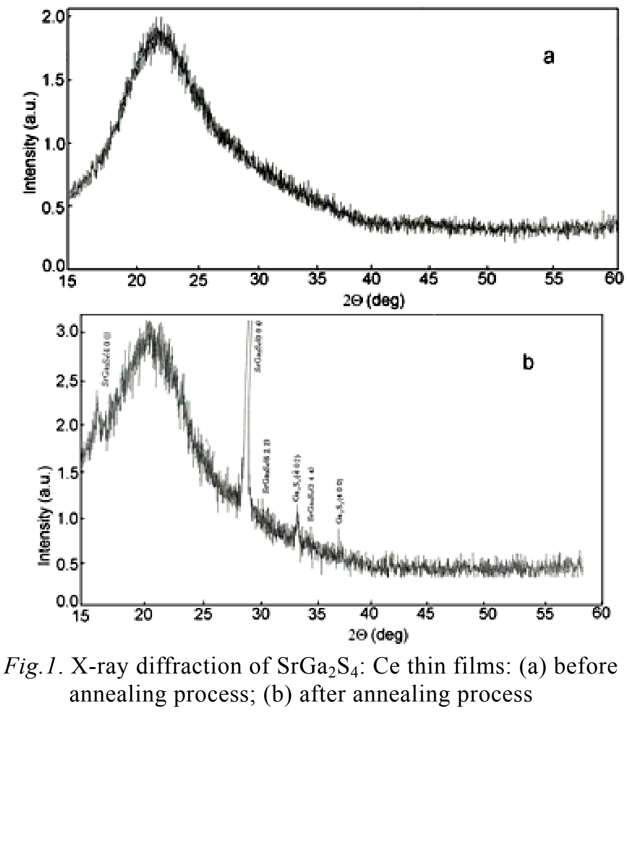

Fig.1. X-ray diffraction of $SrGa_2S_4$: Ce thin films: (a) before annealing process; (b) after annealing process

The annealing of the film leads the appearance of reflection lines; (4 0 0), (6 2 2) and (2 4 4) which are characteristic for $SrGa_2S_4$ compound (see Fig.1b). However, the diffraction curve shows also 2 weak diffraction peaks for Ga_2S_3 compound, (4 0 2) and (4 0 0). The X-ray diffraction results show that the annealing process leads to significant crystallization of obtained amorphous thin films.

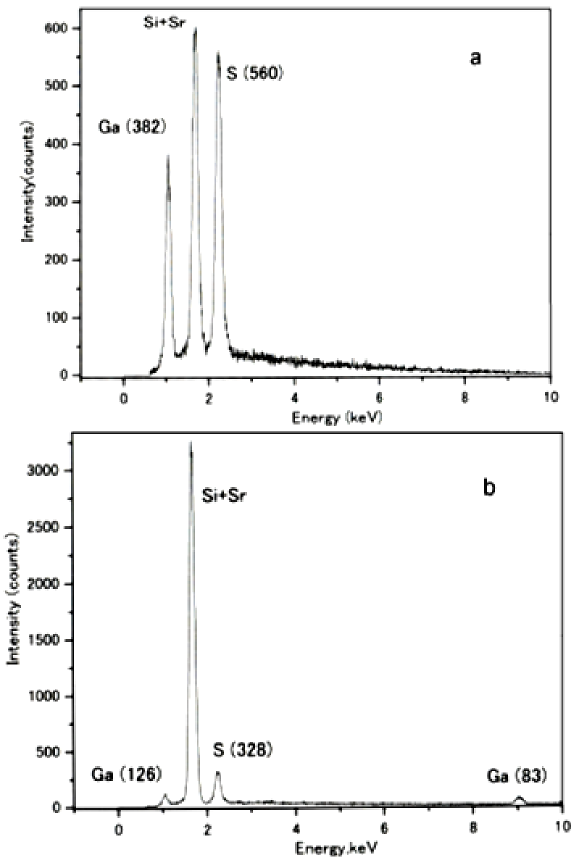

Fig.2. EPMA curve of $SrGa_2S_4$: Ce thin films: (a) before annealing process; (b) after annealing process

The result of an EPMA measurement for the $SrGa_2S_4$ film with thickness of 220 nm is shown in fig.2a. The analytical technique such as EPMA is used to provide a bulk concentration for constituent elements. Before annealing process, there were 3 peaks; Ga, Sr plus Si (Sr+Si) and S. Because of small value of thin film thickness and high energy of incident beam, the electrons penetrated through the films to quartz substrate. Therefore a signal from substrate was also appeared as a Si one. Unfortunately the Sr element cannot be observed because it was overlapped with Si signal from quartz substrate. The ratio between Ga and S intensities before annealing process is 2.0:3.1. From the EPMA result for powder, the ratio between Ga and S was 2.0:4.3 and it is seen that after flash evaporation process thin films possess the significant sulphur deficiency.

For the annealed thin film (see fig.2b), Sr element also cannot be observed because of overlapping with the Si signal. But for the other elements, Ga and S, the intensity ratio was about 2.0:4.1. Comparison with the reference ratio 2.0:4.3 shows that the annealing process leads to essential improvement of film stoichiometry. So, the annealing in 10 % H_2S + 90 % Ar atmosphere reduces the sulphur deficiency in thin films.

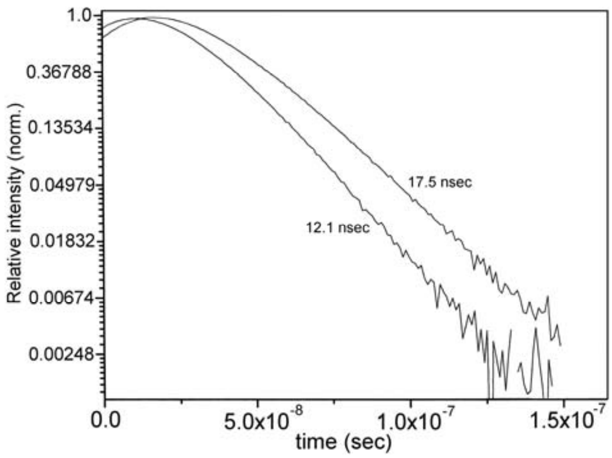

Fig.3. Decay curves of $SrGa_2S_4$: Ce thin film

The results of time decay measurements are shown in fig.3 for the first (450 nm) and the second bands (495 nm) of the photoluminescence spectra [11]. For the first band τ value of film was found to be 12.1 nsec and for the second band was 17.5 nsec.

X-ray studies of $SrGa_2S_4$:Ce thin films showed that immediately after deposition the films exhibited amorphous behavior. The reason of this can be explained by following way. In Ce-doped $SrGa_2S_4$ compound unlike Sr^{2+} ions that are believed to be eightfold coordinated, Ce^{3+} ions (which substitute the Sr^{2+} ions) are surrounded by nine sulphur atoms. The ninth sulphur atom is interstitial one, which is energetically favorable because of charge compensation [3]. The introduction of Ce impurities into $SrGa_2S_4$ leads to (in addition to lattice distortion) occurrence of high concentration of interstitials, which prevent the formation and growth of grains on the substrate during the film deposition. The temperature and duration of deposition process in flash evaporation method are not enough for the crystallization of deposited film. EPMA measurement result shows the sulphur deficiency in "as deposited" films, which can also cause the poor crystallizing of these films. Therefore the thermal treatment of obtained thin films was necessary.

X-ray studies showed that after thermal treatment of films in 10 % H_2S + 90 % Ar stream leads to significant crystallization of amorphous films (fig. 1b). Unfortunately, determination of bulk concentration of constituent elements in thin films using EPMA technique was connected with some difficulties caused by strong overlapping of Sr and Si (quartz substrate) signals. However, the analysis of EPMA results showed that after annealing process the ratio at least between Ga (Ga: as a unit) and S (Ga:S = 1.00:1.95) was close to the ratio 1:2 in the stoichiometric $SrGa_2S_4$ compound within an experimental error. So, the annealing in H_2S atmosphere leads to reduction of sulphur deficiency in thin film.

CONCLUSIONS

For the first time successfully obtained Ce-doped $SrGa_2S_4$ thin film by using flash evaporation method. The main distinctions of this method from the previous methods (DBV, MBE etc.) are the simplicity and cheapness of preparation technology.

Annealing in H_2S gas stream (50 ccm) at 750^0C for 1 hour leads to significant crystallization of the obtained thin films.

The annealing process improves also the stoichiometry of the obtained films.

The characteristic double band blue emission having the maxima at 450 nm and 495 nm can be attributed to short-range order in amorphous phase [11].

The emission decay time of annealed thin films is found to be 12.1 nsec and 17.5 nsec, for the first (450 nm) and the second bands (495 nm), respectively.

The obtained results show that the annealed $SrGa_2S_4$:Ce thin films prepared by flash evaporation method can be used for preparation of electroluminescent cell.

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TERMİK İŞLƏMƏNİN PARTLAYIŞLI BUXARLANMA ÜSULU İLƏ ALINMIŞ $SrGA_2S_4$:Ce NAZİK TƏBƏQƏLƏRİNİN STRUKTUR XASSƏLƏRİNƏ TƏSİRİ

Təqdim olunan hesabatda Ce^{3+} inları ilə aktivləşdirilmiş $SrGa_2S_4$ nazik təbəqələrinin alınma texnologiyası və struktur xassələri verilmişdir.

$SrGa_2S_4$:Ce nazik təbəqələri sadə və bahalı olmayan partlayışlı buxarlandırma üsulu ilə alınmışdır.

Rentgen analizləri göstərir ki, "çökdürülmüş" təbəqələr özlərini amorf kimi göstərir, lakin H_2S mühitində termik işləndikdən sonra polikristal olurlar. Elektron mikroanalizi də nazik təbəqələrin stexiometrik tərkiblərini təsdiq edir.

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ВЛИЯНИЕ ТЕРМИЧЕСКОГО ОТЖИГА НА СТРУКТУНЫЕ СВОЙСТВА ТОНКИХ ПЛЕНОК $SrGA_2S_4$:Ce, ПОЛУЧЕННЫХ ВЗРЫВНЫМ ИСПАРЕНИЕМ

В настоящем докладе приведена технология изготовления и структурные характеристики тонких пленок $SrGa_2S_4$, активированных Ce^{3+}. Тонкие пленки $SrGa_2S_4$: Ce изготовлены так называемым взрывным испарением, которое является простым и недорогим методом для нанесения тонких пленок.

Рентгеноструктурные анализы показывают, что пленки, не подвергшиеся отжигу, обладают аморфным поведением, но после отжига в потоке H_2S они становятся поликристаллическими. Результаты электронного микроанализа подтверждают стехиометрический состав тонких пленок.

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