Molecular-beam epitaxy growth of strontium thiogallate

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The molecular-beam epitaxy growth and characterization of cerium doped strontium thiogallate ($SrGa_2S_4$:Ce) thin film phosphors are reported. The layers were grown on GaAs, and glass/indium tin oxide/dielectric stack substrates for device fabrication. Ga_2S_3/Sr beam equivalent pressure ratios of 20–100 and $CeCl_3$/Sr flux (molecules cm^{-2} s^{-1}) ratios of 1/20–1/10 were investigated in this study. The substrate temperature was varied between 530 and 575 °C. A typical $SrGa_2S_4$:Ce film growth rate of 0.5 μm/h was obtained with Sr, Ga_2S_3, and $CeCl_3$ beam equivalent pressures of 2.0×10^{-7}, 1.0×10^{-5}, and 3.5×10^{-8} Torr, respectively. Characterization of the layers' structural and optical properties by x-ray diffraction, transmission electron microscopy, energy dispersive x-ray spectroscopy, and photoluminescence spectroscopy is presented. *© 1996 American Vacuum Society.*

I. INTRODUCTION

Alkaline earth thiogallates MGa_2S_4 (M=Ca, Sr, or Ba) are wide band gap (4.1–4.4 eV) ternary compounds whose electronic properties and high chemical stability make them ideal host materials for high field electroluminescent (EL) devices. It has been shown that, when doped with cerium, these thiogallates are efficient blue emission phosphors.[1] Thin film thiogallates were first deposited by rf sputtering. However, these films were amorphous and nonluminescent and a post-annealing process at over 750 °C was required to obtain a polycrystalline luminescent film.[2] With sputtering it is difficult to control film composition because usually the film composition differs from that of the sputtering target. Also, high temperature annealing requires the use of high temperature substrates. In molecular-beam epitaxy (MBE) growth, the film stoichiometry and crystallinity can be controlled by changing the growth parameters, such as source material flux ratios and substrate temperature, and it is possible to grow high quality thin films at low temperatures. The MBE growth of cerium doped strontium thiogallate on quartz substrates was first reported in 1994.[3] Here we report growth and characterization results of $SrGa_2S_4$:Ce thin films on low temperature glass and *n*-type (100) GaAs substrates.

II. EXPERIMENT

A modified EPI Modular Gen II system equipped with a Balzers TMU1000 turbo-molecular pump, a custom sample loadlock chamber and 5 sample trolley system was employed for this research. Reflection high energy electron diffraction (RHEED) was used as an *in situ* monitor of the film crystalline structure and surface morphology, and also served as a means of qualitatively assessing the luminescent properties of the films. The substrate temperature was determined by a spring loaded thermocouple pressed against the back of the substrate holder and was calibrated by the appearance of a crystalline RHEED pattern due to the removal of the amorphous oxide layer on a GaAs substrate at 581 °C. The background pressure of the system was 5.0×10^{-9} and 5.0×10^{-7} Torr before and during deposition, respectively.

For growth, Sr, Ga_2S_3, and $CeCl_3$ compounds were sublimed from conventional effusion cells with pyrolytic boron nitride (PBN) crucibles and were monitored by a quadrupole mass spectrometer. It was found that at the operation temperature of the Ga_2S_3 cell (~950 °C), Ga_2S_3 sublimed as Ga_2S and S_2 in agreement with the observations of Kashkooli *et al.*[4] and Mills.[5] GaAs (100) was used as a crystalline substrate for high quality epitaxial layer deposition and glass/indium tin oxide(ITO)/dielectric stack substrates were used for EL device fabrication. Ga_2S_3/Sr beam equivalent pressure (BEP) ratios of 20–100 and $CeCl_3$/Sr flux (molecules cm^{-2} s^{-1}) ratios of 1/20–1/10 were investigated in this study for substrate temperatures ranging from 530 to 575 °C.

The crystallinity of the thiogallate thin films was analyzed using a Philips PW1800 automatic powder diffractometer (Cu Kα) and the atomic structure of the films grown on GaAs substrates determined using high-resolution transmission electron microscopy (HRTEM) with a Hitachi HF-2000 cold field emission gun transmission electron microscope (200 kV). The high brightness and highly coherent source of this TEM allows high-resolution structure imaging at a point-to-point image resolution better than 0.23 nm and a lattice resolution of 0.1 nm. The chemical composition of the films was determined by energy dispersive x-ray spectroscopy (EDX) and the cerium doping concentration was determined by secondary ion mass spectroscopy (SIMS). The optical properties of the phosphor films were analyzed by photoluminescence (PL) measurements using the 275 nm argon ion laser line. The PL signal was dispersed by a SPEX 1000M monochromator and detected by a thermoelectrically cooled GaAs photomultiplier tube. EL devices were fabricated from the films deposited on glass substrates and characterized.

III. RESULTS AND DISCUSSIONS

It was found that the structural properties of the $SrGa_2S_4$ films were strongly dependent on the Ga_2S_3/Sr flux ratio and

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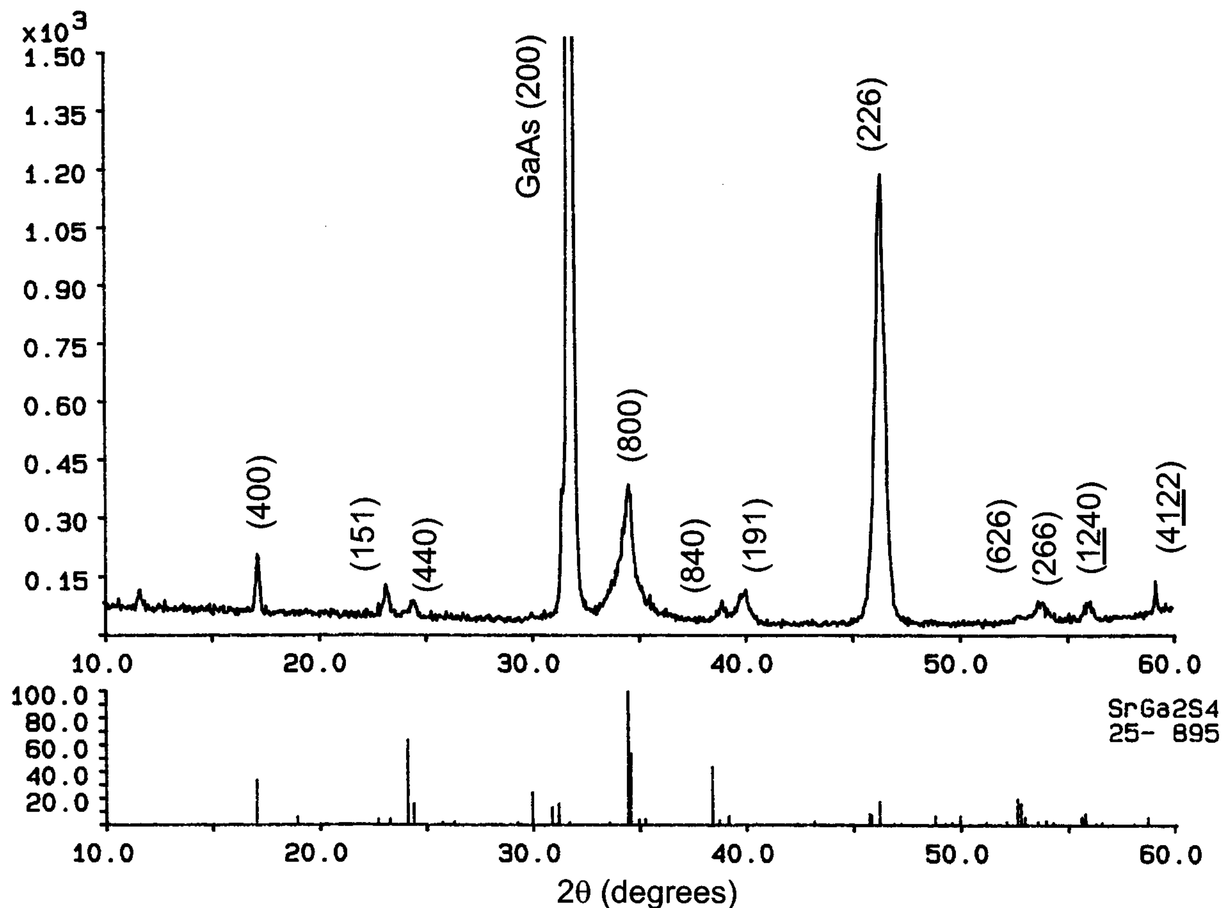

FIG. 1. X-ray diffraction spectrum of a $SrGa_2S_4$:Ce film on GaAs substrate (top) with standard powder $SrGa_2S_4$:Ce diffraction pattern (bottom).

substrate temperature. For the range of deposition conditions investigated, it was found that the optimum conditions for single phase polycrystalline $SrGa_2S_4$ film growth were substrate temperatures between 550–560 °C and Ga_2S_3/Sr BEP ratios of 50–60. The growth rate of single phase $SrGa_2S_4$ was observed to be proportional to the Sr flux. A typical $SrGa_2S_4$:Ce film growth rate of 0.5 μm/h was obtained with Sr, Ga_2S_3, and $CeCl_3$ BEPs of 2.0×10^{-7}, 1.2×10^{-5}, and 3.5×10^{-8} Torr, respectively, at 550 °C.

Figure 1 shows an x-ray diffraction (XRD) pattern of a $SrGa_2S_4$ film deposited on a GaAs substrate grown at 550 °C with a Ga_2S_3/Sr BEP flux ratio of 60. From comparisons with the standard powder pattern for $SrGa_2S_4$, all of the peaks were found to belong to orthorhombic $SrGa_2S_4$, indicating the single phase polycrystalline structure of the film. The dominant peak is the (226) reflection, indicating a preferred crystal orientation or textured structure. Similar results were obtained for deposition on glass substrates. The XRD spectra of films grown at 550 °C with a high Ga_2S_3/Sr BEP flux ratios of over 100 and films grown at adequate flux ratio, but at a low substrate temperature, showed an extra GaS phase. In contrast, films grown at 550 °C with Ga_2S_3/Sr BEP flux ratios lower than 20, and films grown at an adequate flux ratio but at temperatures above 575 °C exhibited a SrS phase in addition to the $SrGa_2S_4$ phase.

From the experimental observations and the thermodynamic properties of the related compounds, the following growth model is proposed. As mentioned previously, the Ga_2S_3 sublimed as

$$Ga_2S_3(s)=Ga_2S+S_2. \quad (1)$$

Thus, the compounds reaching the growth surface are Ga_2S, S_2, and Sr. Because of the low vapor pressure of SrS in the substrate temperature range investigated,[6] the following reaction is proposed. At low excess Ga_2S and S_2 fluxes

$$2Sr+Ga_2S+S_2=2SrS+Ga_2S\uparrow. \quad (2)$$

The formation of the SrS layer is also supported by the fact that SrS is deposited by MBE at temperatures higher than those used in this study.[7] Following the formation of SrS on the substrate, as the Ga_2S and S_2 fluxes are increased further the following occurs to form the strontium thiogallate film:

$$SrS+Ga_2S+S_2=SrGa_2S_4. \quad (3)$$

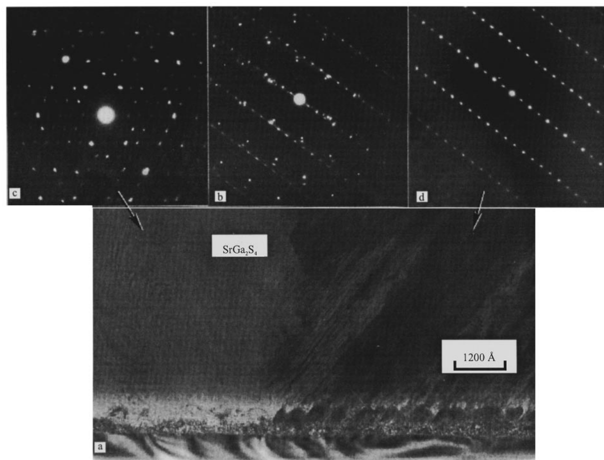

FIG. 2. (a) Low magnification cross-section TEM image of $SrGa_2S_4$:Ce/GaS_2/GaAs and (b) an electron diffraction pattern of the film showing epitaxial growth of the deposited film. (c) and (d) are electron diffraction patterns recorded from the left- and right-hand side, respectively, of the $SrGa_2S_4$:Ce film shown in (a).

The above reaction occurs at the optimum growth conditions which have been experimentally determined as a Ga_2S_3/Sr ratio of 50–60 and a substrate temperature of 550–560 °C. At a lower flux ratio, there will be an excess of SrS compared to Ga_2S and S_2 for reaction (3). Also, if the substrate temperature is increased, the Ga_2S and S_2 desorption rates increase because of their relatively high vapor pressures. In both cases, a secondary SrS phase will appear in the film as observed by XRD. On the other hand, higher flux

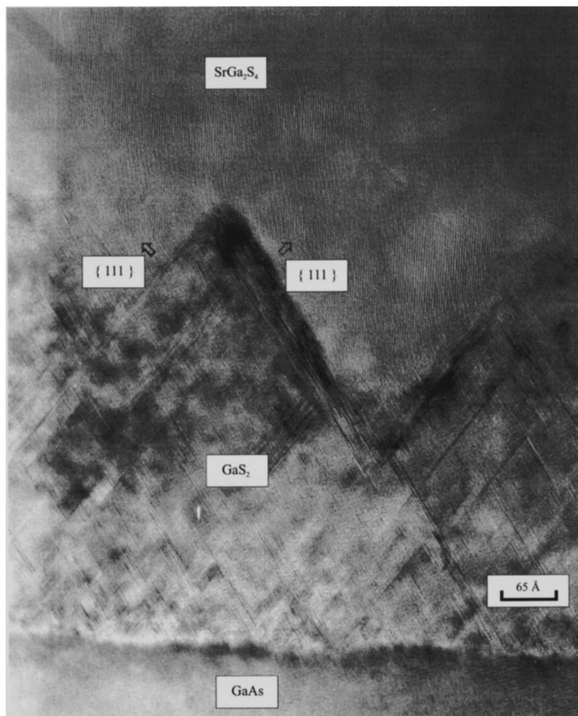

FIG. 3. High-resolution TEM image of $SrGa_2S_4$:Ce/GaS_2/GaAs epitaxial film.

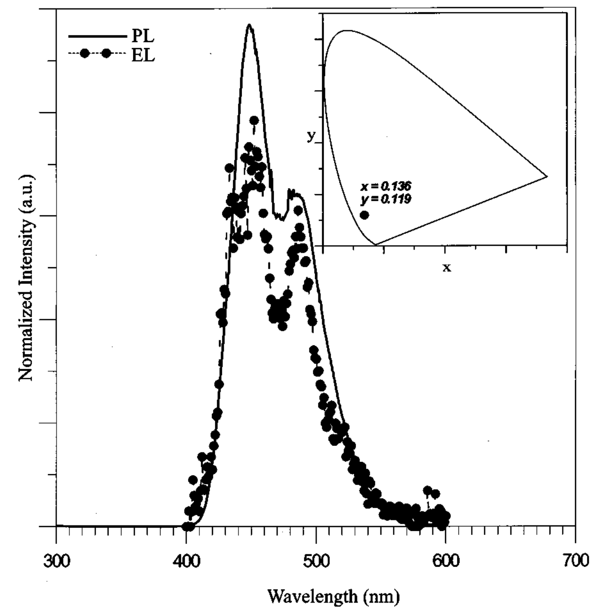

FIG. 4. Room temperature electroluminescent and photoluminescence spectra of $SrGa_2S_4$:Ce thin film. The dotted line represents the electroluminescent spectrum of a device made with this $SrGa_2S_4$:Ce thin film phosphor. The inset depicts the CIE color coordinates for this film.

ratios supply more Ga_2S and S_2 than SrS and lower substrate temperatures reduce the Ga_2S desorption rate in reaction (2). Under these situations, following reaction can occur:

$$2Ga_2S+2S_2=4GaS+S_2\uparrow. \quad (4)$$

As a result, a GaS phase appears in the film in addition to the $SrGa_2S_4$. The $CeCl_3$ source supplies the Ce^{3+} activator ions and Cl^- ions which supply charge compensation for the Ce^{3+} which substitute for Sr^{2+} ions.[8]

Figure 2(a) shows a low magnification cross-sectional TEM image of an $SrGa_2S_4$/GaS_2/GaAs film, in which the substrate, GaS_2 buffer layer and $SrGa_2S_4$ film are clearly resolved. The electron diffraction pattern recorded from the region, as shown in Fig. 2(b), indicates epitaxial growth of the film. The GaS_2 layer shows the same crystal orientation as the GaAs substrate. The two grains shown in Fig. 2(a) are $SrGa_2S_4$, as confirmed by EDX microanalysis, although they appear in different contrast. The electron diffraction patterns, Figs. 2(c) and 2(d), recorded from these two regions show distinct crystal orientations, which are consistent with optical microscopy observations. Figure 3 is a high resolution lattice image of the $SrGa_2S_4$/GaS_2/GaAs film. The epitaxial relationship is apparent. Numerous {111} stacking faults are observed in the GaS_2 layer, some of which are directly initiated from the GaS_2/GaAs interface, resulting in the growth of a pyramidlike structure with {111} facets.

In this study, a GaS_2 phase rather than the GaS phase was observed by EDX in the buffer layer. As shown in Fig. 3, a high density of stacking faults was observed in the GaS_2 layer although the nature and local chemistry of the faulted layer is unclear, it is possible that the stacking faults are S

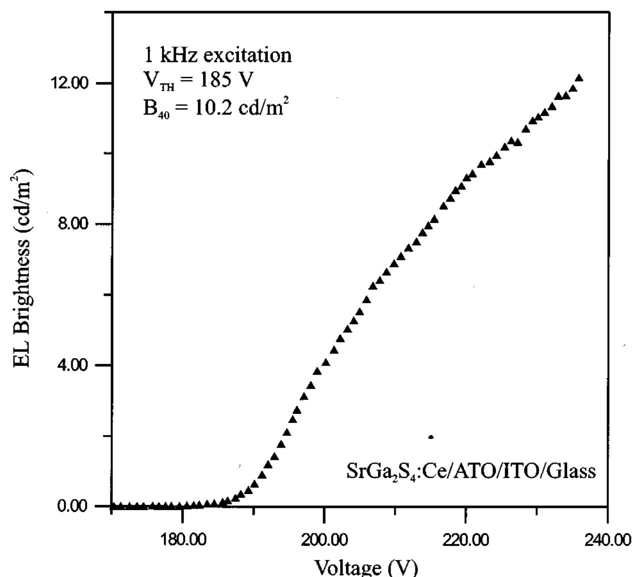

FIG. 5. The brightness vs voltage curve of the $SrGa_2S_4$:Ce electroluminescent device under 1 kHz excitation.

rich. Moreover, the GaS_2 may be a stable phase for a thin film layer in the chemical environment considered here. More experimental studies are planned to identify the nature of the GaS_2 phase and its relationship with the observed stacking faults. The EDX results confirmed the stoichiometric ratios of the $SrGa_2S_4$ film, within experimental error (i.e., Sr:Ga:S=1:2:4). Also SIMS measurements indicated the cerium atomic concentration to be 1%.

Bright blue emission was observed from room temperature PL measurements. As shown in Fig. 4, two broad emission bands centered at 449 nm and 485 nm were observed and assigned to the $^2D \rightarrow ^2F_{5/2}$ and $^2D \rightarrow ^2F_{7/2}$ transitions of the Ce^{3+} ions, respectively. The Commission International de l'Eclairage (CIE) color coordinates obtained from the spectrum were $x=0.136$ and $y=0.119$.

Figure 5 shows the brightness versus voltage curve of an EL device under 1 kHz excitation. This device exhibited a threshold voltage of 185 V, and a brightness of 10.2 cd/m^2 at 40 V above threshold, with a maximum brightness of 12.8 cd/m^2. The same device, when operated at 60 Hz, shows a threshold voltage of 187 V, a brightness of 0.77 cd/m^2 at 40 V above threshold and a maximum brightness of 0.97 cd/m^2. As also indicated in Fig. 4, the EL spectrum is similar to the PL spectrum, but gives slightly different color CIE coordinates, of $x=0.158$ and $y=0.129$. This chromaticity is comparable to that of blue cathode-ray tube (CRT) phosphors.

IV. CONCLUSION

The optimum MBE growth conditions of cerium doped strontium thiogallate have been identified as a Ga_2S_3/Sr BEP ratio of 60–70 at a substrate temperature of 550–560 °C. $SrGa_2S_4$ films have been grown under these optimized conditions on both GaAs and low temperature glass/ITO/dielectric stack substrates. The as-deposited film are epitaxially grown on the substrate/buffer layer, and have a single phase polycrystalline structure with the correct stoichiometric ratio. Further optimization of buffer/interface layers could lead to improved EL device efficiency and brightness.

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