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Triboluminescence of ZnS:Mn films deposited on Ceramic Substrates

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We have grown highly oriented ZnS:Mn films on SiC and alumina substrates by rf magnetron sputtering method. The effect of annealing on the triboluminescence and photoluminescence was investigated. Annealing the films in 5% H_2 diluted in Ar, the crystallinity and triboluminescence intensity of the films were greatly improved. Such a device can be used in the new mechan-optic applications such as stress sensors or the detection of fracture in micro-and macro-scales.
Key words: Triboluminescence, Photoluminescence, Annealing, ZnS films

1. INTRODUCTION

Luminescence processes can be classified according to the type of radiation/energy used to excite the emission. Well known luminescence phenomena such as photoluminescence, which is excited by visible or ultra violet light, electroluminesence, which is excited by an electric field and cathodoluminescence, excited by an energetic electron beam. Triboluminescence (TrL) is another luminescence phenomenon in which light is emitted due to the application of a mechanical energy [1]. TrL is observed during a wide variety of situations involving solid objects such as collision, striking, friction and grinding [1-4]. This stress-related, photon-emitting capabilities of materials when developed can be used as stress sensors or the detection of fracture in micro-and macro-scales. Many materials exhibit TrL, however, the emitted light in most materials is too weak to detect. In previous studies [5-10], the crystallinity and luminescence properties of ZnS:Mn films on quartz glass substrates were found to be improved by postannealing at higher temperatures. Until now, ZnS:Mn TrL research has been concentrated on bulk or powder and thin films on quartz-glass substrates and to our knowledge no intensive study has been reported on the TrL of ZnS:Mn films on ceramic substrates.

In order to realized practical applications based on this phenomenon, it is important to study the behavior of ZnS:Mn films on ceramic substrates such as SiC. In this work, ZnS:Mn films were grown by rf sputtering method on SiC and Al_2O_3 substrates and annealed at various temperatures in 5 % hydrogen diluted in Ar.

2. EXPERIMENTAL PROCEDURE

The ZnS:Mn films deposited on the SiC and Al_2O_3 substrates were grown by the rf magnetron sputtering method. The optimum sputtering conditions used in the deposition of the ZnS:Mn films shown in Table 1 were obtained from a statistical approach [11]. The sputtering system had a normal sputtering chamber with a sintered ZnS:Mn (99 %: 1 %) target, 7 cm in diameter kept at a distance of 8 cm from the substrate holder. The SiC and Al_2O_3 substrates used were cleaned using a conventional cleaning procedure. The growth chamber was evacuated by a connection of an oil-free turbomolecular and rotary pumps before admitting high purity argon gas (99.99 %) into the chamber. A thermocouple embedded in the core of the substrate holder was used to monitor the substrate temperature during sputtering. As-grown films were annealed at 600 °C, 700 °C and 800 °C for 1 h in 5 % H_2 diluted in Ar ambient.

The resultant film thickness was measured by a conventional surface roughness detector with a stylus on partially coated substrates. The crystal structure of the film was determined by an X-ray diffractometer (RINT2000, Rigaku) using CuKα radiation. The photoluminescence spectrum of the films was measured by a fluorescence spectrophotometer (Jasco FP-6500) at room temperature. A photon counting system was used to measure the TrL intensity induced by mechanical friction that was produced by rotating a 1mm diameter plastic rod (150 rpm) with a load of 2N (7,8), which consist of a photo multiplier tube (model R464S, Hamamatsu Photonics, Hamamatsu, Japan) and a photon counter (model C5410-51, Hamamatsu Photonics) controlled by a computer.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns (θ-2θ scan) of SiC substrate and ZnS:Mn films on SiC substrate annealed in 5 % H_2 diluted in Ar at various temperatures. The presence of the (111) peak in the as-grown and annealed ZnS:Mn films shows that the films are oriented along the c-axis direction. As compared to the SiC substrate, the as-grown and the annealed films showed the (111) and the (222) peaks due to the ZnS films whilst the remaining peaks are attributed to the SiC substrate. The dominant (111) peak and (222) peak also appeared in the XRD patterns when ZnS:Mn films were deposited on Al_2O_3 substrates.

Figure 2 also shows the relationship between the annealing temperature and the full width at half maximum (FWHM) of the (111) peak of ZnS:Mn films on SiC and Al_2O_3 substrates. The FWHM values of an XRD peak depends on the crystallite size and the lattice

Table 1. Sputtering conditions used

Substrate temp.	150 °C
Rf power	180 W
Sputtering press.	1.5 Pa
Sputtering time	90 minutes
Target diameter	7 cm

strain caused by defects or dislocations [12]. Therefore, FWHM values can be used to evaluate crystallinity: that is the smaller the FWHM, the greater the crystallinity. It can be seen that, the crystallinity of the films improved with the increase in the annealing temperature. The minimum FWHM value was obtained when the films were annealed at 700 °C. After 700 °C, the crystallinity of the films on both substrates depreciated, due to the sublimation of the film at high temperature.

Figure 3 shows the room temperature PL spectra of as-grown and annealed ZnS:Mn films on Al_2O_3 substrates. The excitation wavelength used was 340 nm. The as-grown film showed no visible emission, but an emission peak around 580 nm was detected when the films were

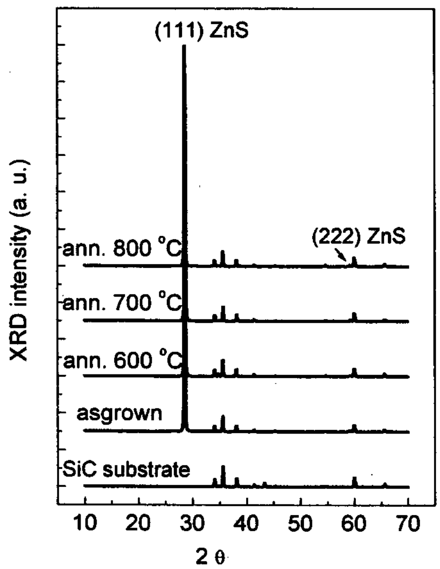

Fig. 1 XRD patterns of SiC substrate and as-grown and annealed ZnS:Mn films on SiC substrate.

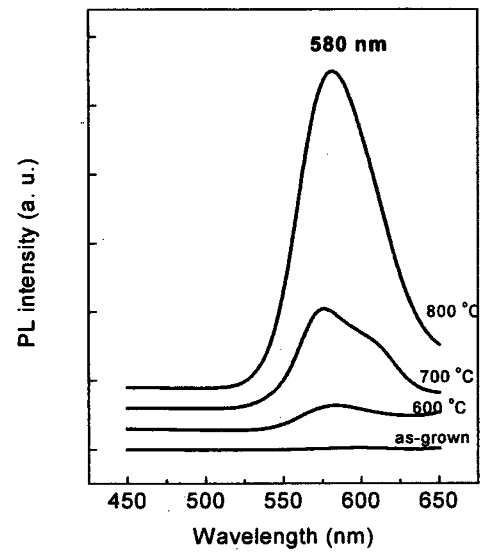

Fig. 3 Room temperature PL spectra of as-grown and annealed ZnS:Mn films on Al_2O_3 substrates.

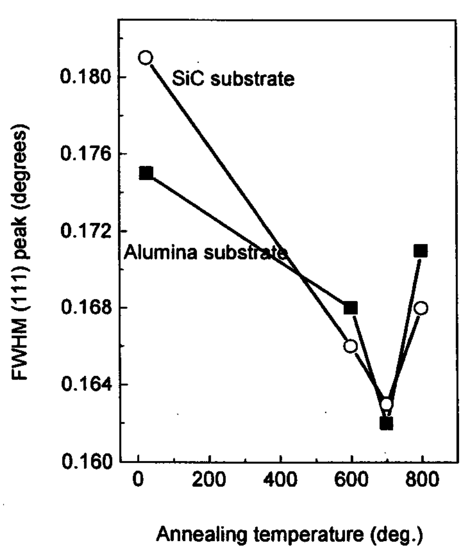

Fig. 2 Relation between annealing temperature and the FWHM of the (111) ZnS peak on SiC and Al_2O_3 substrates.

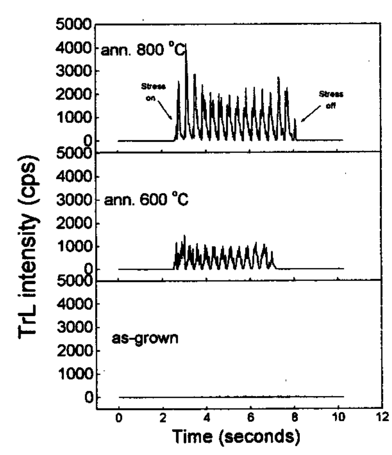

Fig. 4 TrL-Time curves for as-grown and annealed ZnS:Mn films on alumina substrates.

annealed at 600 °C. The intensity of this peak increased up to 800 °C. This emission peak is due to the $^4T_1(G) \rightarrow {}^6A_1(S)$ transition within the 3 d shell of Mn^{2+}[13,14]. ZnS:Mn is an important electroluminescence phosphor used as thin films. Experiments in photoelectron spectroscopy revealed that the position of the Mn^{2+} ground state is located 3.5eV below the top of the valence band [15]. When UV radiation is applied, it is enough to cause the excitation of electrons within the 3 d shell of the Mn^{2+}. Both photoluminescence (PL) and triboluminescence (TrL) are luminescence phenomena but they differ in the mode of the excitation mechanisms. Similar results were also obtained for ZnS:Mn films on SiC substrates.

Figure 4 shows the TrL-time curves for as-grown and annealed ZnS:Mn films on alumina substrate on the same scale. As explained earlier, the TrL intensity was obtained by rotating a plastic rod on the film surface and the emitted lights were detected by a photon counting system. The TrL intensity was very low for the as-grown film, but the intensity greatly improved with the

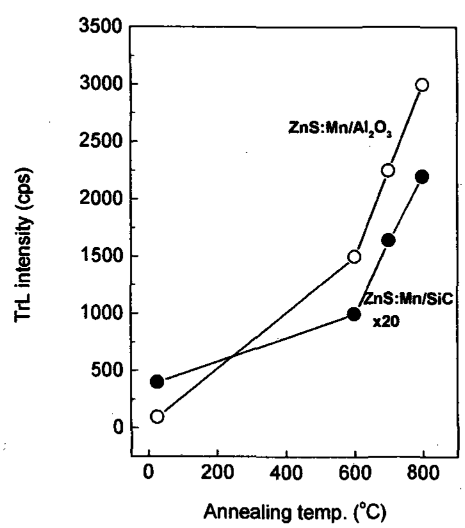

Fig. 5 Relation between the TrL intensity and annealing temperature for ZnS:Mn films on SiC and Al_2O_3 substrates.

annealing up to a maximum at 800 °C. Beyond 800 °C, there is complete sublimation of the film from the substrate. In previous study [10], the TrL intensities of ZnS:Mn films on quartz substrates annealed in 5% H_2 diluted Ar were found to increase in intensity up to 700 °C. At 800 °C, film sublimation greatly affected the TrL intensity. We have been able to achieve higher TrL intensity on ceramic substrate at 800 °C, which is very encouraging in realizing practical ZnS:Mn TrL films.

Figure 5 shows the relation between the TrL intensity and the annealing temperature for ZnS:Mn films on SiC and alumina substrates. It can be seen that, the TrL intensity of the film on both substrates increased with increasing annealing temperature but the TrL intensity on the alumina substrates were very high compared to that of the SiC substrates. In the case of SiC and alumina substrates we still have a high increase in TrL intensity at 800 °C. At 900 °C, the crystallinity of the films may reduce drastically and the films may sublimate completely from the substrate.

CONCLUSION

ZnS:Mn films have been grown on SiC and Al_2O_3 substrates by rf magnetron sputtering method. Oriented ZnS:Mn films were obtained on both substrates and their crystallinity improved by annealing the films in 5% H_2 diluted in Ar up to 700 °C. The single emission peak (around 580 nm) in the room temperature PL spectra and the TrL intensities of the films greatly improved upon annealing up to 800 °C. This is the first time that TrL in ZnS:Mn films on ceramic substrates has been investigated.

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