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DEVELOPMENT OF STRONG TRIBOLUMINESCENCE ZnS:Mn FILMS ON VARIOUS GLASS SUBSTRATES

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Highly oriented and crystallized films of ZnS:Mn were successfully deposited on various glass substrates (Pyrex, quartz, β-SiO_2 etc) under an optimized sputtering conditions. All the films were then annealed at 700^{0}C in 5% H_2 diluted in Ar ambient and detailed study of their triboluminescence (TrL) intensities, surface roughness, film adhesion and crystallinity in relation to the annealing temperature was carried out. It was found out that, ZnS:Mn/quartz system exhibited high TrL and strong mechanical strength and therefore can be used as a stress/friction sensor for various applications.

Key words: Triboluminescence, ZnS, Thin Film, Adhesion.

1. INTRODUCTION

Zinc Sulfide (ZnS) is a wide band-gap semiconductor (3.6-3.7eV) used in many applications such as phosphors [1], solar cells [2] and IR windows [3]. Films of ZnS doped with manganese (ZnS:Mn) are also the active layers of both ac and dc addressed thin film electroluminescent (TFEL) devices [4]. Besides these optoelectronic applications, we are also interested in the new mechano-optical application, where it has been found that ZnS:Mn films is a promising material to emit intense light upon stress, a phenomenon known as triboluminescence (TrL) [5-8]. Many crystals exhibit TrL, however, the emitted light in most materials is too weak to detect. In addition, as-deposited polycrystalline ZnS:Mn films often exhibit poor crystallinity and inferior luminescent properties, requiring postannealing at high temperatures to improve the crystallinity of the host material (ZnS) and to control the oxidation state and crystal symmetry of the activator (Mn) in order to achieve high performance luminescent characteristics. We have analyzed the effects of thermal annealing on the TrL intensity of sputtered ZnS:Mn films on a particular quartz substrate and found that, the highest TrL intensity was obtained when the films were annealed in Ar/H_2 ambient at 700^{0}C [9]. In this work, we have studied the TrL intensity of sputtered ZnS:Mn films on various quartz/glass substrates annealed at 700^{0}C in Ar/H_2 ambient. The film crystallinity and adhesion strength of the as-grown and annealed films were also studied.

2. EXPERIMENTAL

The sputtering conditions of the ZnS:Mn films used in this work had been obtained earlier from a statistical approach[10]. In that work, the substrate temperature was found to be the most significant control factor for the deposition of oriented ZnS:Mn films. Six (6) substrates labeled G1 (TPX, hard glass), G2 (Ceramu, crystallized glass), G3 (β-SiO_2), G4 (fused quartz), G5 (synthesized quartz) and G6 (optical glass) were used. The substrates were ultrasonically cleaned in acetone, deionised water and ethanol before loading them into the growth chamber. The target was made up of ZnS (99%) doped with Mn (1%). The growth chamber was evacuated by a connection of an oil-free turbomolecular and rotary pumps before admitting a high purity Argon gas (99.99%). As-grown films were annealed at 700°C for 1 hour in 5% H_2 diluted in Ar ambient. The film thickness was determined by surface profilometry on partially coated substrates. The crystal structure of the films was determined by an X-ray diffractometer (RINT2000, Rigaku) using CuKα radiation. A photon counting system was used to measure the TrL intensity induced by mechanical friction that was produced by rotating a 1 mm diameter plastic rod (150 rpm) with a load of 2N [11]. It consisted of a photon multiplier tube (model R464S, Hamamastu Photonics, Hamamastu, Japan) and a photon counter (model C5410-51, Hamamastu Photonics) controlled by a computer. The adhesion strength of the film was evaluated by a universal adhesion tester with a built-in acoustic emission (AE) sensor (model Romulus II, Adhesion International, Spokane, WA).

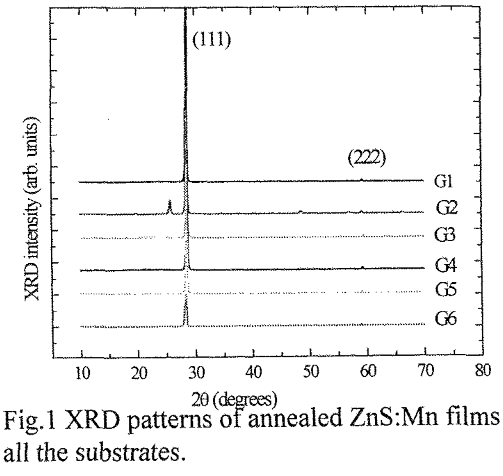

Fig.1 XRD patterns of annealed ZnS:Mn films on all the substrates.

Table I, Properties of ZnS:Mn films on all the substrates. Figures in parenthesis are for annealed samples.

Subt.	Rough (μm)	FWHM (deg)	Cryst. sizeÅ	Thick. (μm)
G1	0.07 (0.45)	0.192 (0.173)	650.94 (867.10)	1.1 (deform)
G2	0.08 (0.29)	0.182 (0.182)	745.43 (745.43)	1.2 (deform)
G3	0.06 (0.06)	0.180 (0.173)	769.42 (867.10)	0.8 (0.8)
G4	0.07 (0.07)	0.180 (0.173)	769.42 (867.10)	1.2 (1.2)
G5	0.05 (0.05)	0.182 (0.173)	745.43 (867.10)	0.8 (deform)
G6	0.06 (0.14)	0.190 (0.183)	665.63 (733.21)	0.8 (deform)

Table II, Mechanical strength and TrL intensity of the films on all the substrates.

Glass/quartz	Fracture point(N)	TrL int. (cps)
G1	4.5	882
G2	6.0	1142
G3	9.9	3316
G4	15	5298
G5	8.2	985
G6	-	-

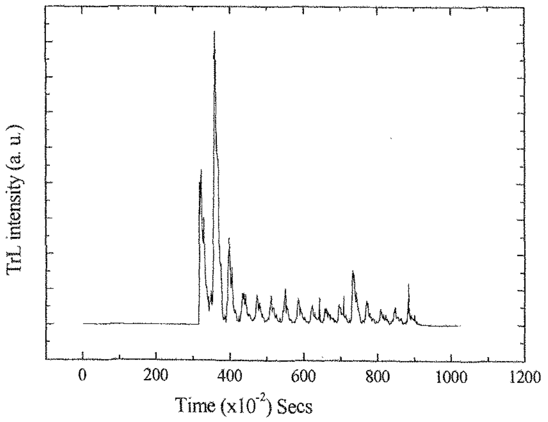

Fig.2 Typical TrL intensity-time curve for ZnS:Mn films on a quartz substrate.

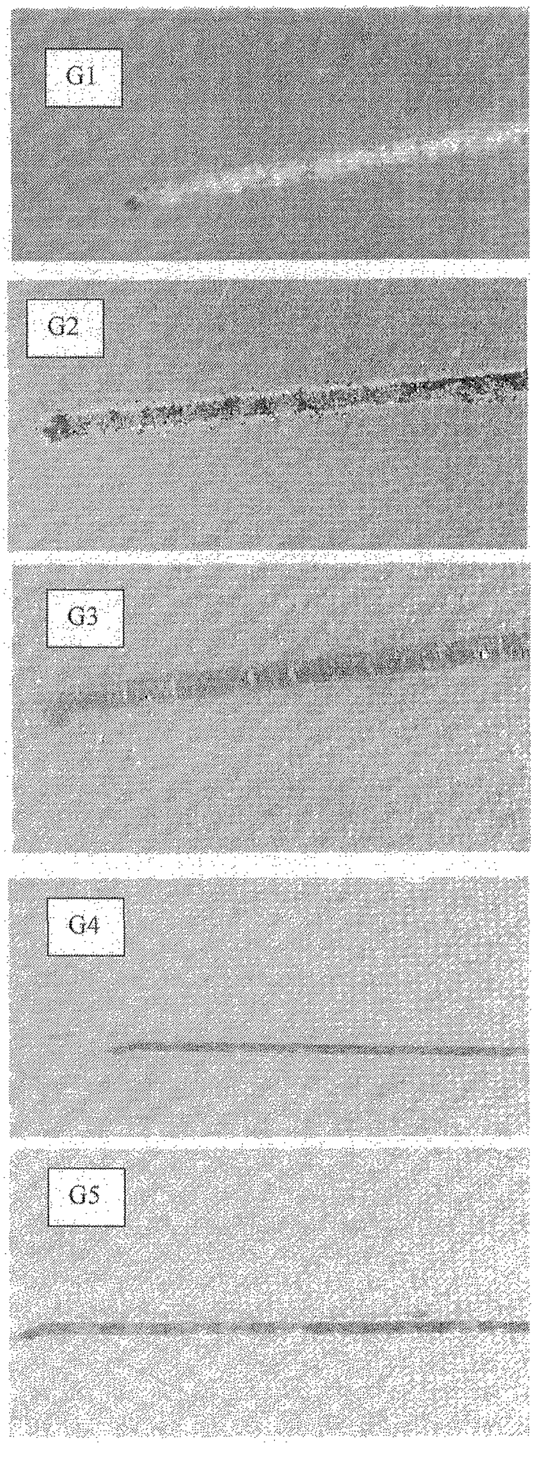

Fig.3 Optical micrographs of film surfaces after the adhesion measurements.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern (θ-2θ scan) of the ZnS:Mn films on all the substrate annealed (700^0C in 5%H_2/Ar) for 1 hour. The presence of the dorminant (111) peak on all the substrates shows that the ZnS:Mn films has well defined crystal orientation, where the c-axis direction is perpendicular to the substrate plane. The additional peaks appearing only on the G2 substrate were all confirmed from the G2 substrate itself. Table 1 shows the FWHM, thickness, crystallite size and the roughness values of the as-grown and annealed films on all the substrate. The full-width at half maximum (FWHM) of an XRD peak depends on the crystallite size and the lattice strain caused by the defects or dislocations [12]. Therefore, FWHM values can be used to evaluate crystallinity: that is the smaller the FWHM value the greater the crystallinity. The crystallite size was estimated from the Scherrer formula; $t = 0.9\lambda$ /B $\mathrm{Cos}\theta_B$, where B is the FWHM (in radians), λ is the x-ray wavelength (Å) and t is the crystallite size (Å). The corrected FWHM values used in the Scherrer's equation are obtained when the XRD of a standard sample is measured to determine the known FWHM. Subtraction of the known FWHM value from the unknown ($B^2 = U^2 - S^2$) gives the value for the corrected FWHM used in the Scherrer's equation. In our case, the standard sample used was a Silicon powder with a peak position at 28.36^0 and an FWHM of 0.145^0. From Table 1, it can be seen that the values of the crystallized sizes estimated were much larger than 500Å, the limitation for such a method, thus the estimated size in Table 1 was not of high reliability. The annealing also affected the surface roughness of the films on some substrates such as G1, G2 and G6. Whilst G6 was curved after annealing at 700^0C, it was very difficult to measure the film thickness. The surface roughness of the films on G3, G4 and G5 was almost the same after annealing at 700^0C. High annealing affected the film-substrate adhesion making it impossible to measure the film thickness of G1, G2, G5 and G6. The film thickness for G3 and G4 were almost the same after annealing at 700^0C.

Figure 2 shows a typical TrL intensity-time curve for ZnS:Mn films on a quartz surface. The decrease in the TrL intensity with time is due to the peeling of the films from the substrates. Table 2 shows the critical load values of the failure points obtained from the AE sensor and optical microscopy. In this method, a stylus with an increasing load is drawn over the film surface at a constant speed. The scratch test unit is equipped with an acoustic detector mounted directly above the stylus in such a way that, acoustic emission accompanying the adhesive failure of the film-substrate can be recorded as the scratches are made. Figure 3 shows the optical micrographs of the nature of the scratch path on the annealed films on all the substrates after the adhesion measurement. The complete destruction of the films by the stylus illustrates a weak adhesive film. From Table 2 it can be seen that G3 and G4 substrates exhibited a strongly adherent film whilst it can be seen that the rest is poorly attached to the film. G6 substrate was badly deformed in such a way that we could not measure both the TrL intensity and adhesion strength of the film. These results also shows the value of combining the data from the scratch test with optical microscopy to build up a more complete understanding of the failure mechanisms in such film-substrate system. We are still working on the dependence of the film properties on each substrate. We are measuring the thermal expansion coefficients for each substrate within the annealing range to see if there is a correlation between the film properties and each substrate. X-ray rocking curves about the (111) peaks were measured for both as-grown and annealed films and the FWHM of the rocking curves were deduced. The FWHM values obtained showed no distinguish changes for both as-grown and annealed films, thus the degree of crystal orientation had not been modified by the annealing technique. Results also shows that G4 and G3 substrates are promising materials for ZnS:Mn films for triboluminecsence applications.

4. CONCLUSION

We have analyzed ZnS:Mn films on different quartz/glass substrates grown by rf sputtering technique and annealed (5% H_2 in Ar) for 1 hour at 700^0C . We realized that films grown on G3 and G4 substrate withstood higher annealing temperature and exhibited a strong mechanical strength. We still need to work on the TrL intensity and film adhesion of these films in order to realize the mechano-optical applications based on this phenomenon.

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