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Optimization of Sputtering Conditions of Zinc Sulfide Thin Films on Ceramic Substrates for Novel Triboluminescence Application

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A statistical method of the design of experiments and analysis of variance (ANOVA) has been used to obtain optimized sputtering conditions for oriented zinc sulfide thin films doped with 5% manganese on glass substrates. The effects of the five sputtering factors; substrate temperature, rf power, sputtering pressure, sputtering time and pre-sputtering time were simultaneously investigated by using the design of experiment and ANOVA. Through only 16 experiments, it has been proved statistically at the 5% level that the substrate temperature is the only significant control factor. Zinc sulfide films were then deposited under the optimized sputtering conditions on other polycrystalline substrates. Oriented ZnS: Mn films with high crystallinity were obtained on various substrates such as alumina, silicon nitride, silicon carbide and carbon. Their photoluminescence (PL) and triboluminescence (TL) at 300 K were studied. Both PL and TL intensities were found to be enhanced with the increasing of crystallinity of ZnS by means of post-annealing.

Key words: Zinc sulfide, Thin film, Photoluminescence, Triboluminescence

1. INTRODUCTION

Being a II-VI semiconductor, zinc sulfide has found many applications in various fields such as phosphors [1], solar cells [2] and IR windows [3]. Films of zinc sulfide doped with manganese (ZnS:Mn) are of particular interest to be the active layers of both ac and dc addressed electroluminescent devices [4]. Besides these optoelectronic applications, we are also interested in the new mechano-optical application of ZnS. So far we have found that ZnS:Mn thin film is a promising candidate to emit intense light upon stress which is known as triboluminescence (TL) phenomenon, and found that the crystalline nature of the host material of ZnS greatly influenced the luminescence properties [5].

Various chemical and physical methods can be used for the deposition of films of ZnS:Mn, among which radio frequency (rf) sputtering is an attractive production technique [6]. Using this technique, the crystallinity of films greatly depended on many sputtering factors, such as substrate temperature, rf power, sputtering pressure, etc. Hence the optimization of sputtering conditions needs a large number of experiments. Design of experiments and analysis of variance (ANOVA) are mathematical statistical methods that will reduce the number of experiments, show the effect of a control factor and then gives the optimum sputtering conditions [7-9]. For example, to investigate five sputtering control factors with four levels, only 16 experiments would be sufficient to obtain the optimum sputtering conditions by using design of experiments $L16(4^5)$ and ANOVA.

In this study, we investigated the significance of five sputtering factors; substrate temperature, rf power, sputtering pressure, sputtering time and pre-sputtering time on the crystallinity of ZnS:Mn films on glass substrates. The dependence of the film crystallinity on the substrate temperature was investigated in more detail, because the substrate temperature was found to be the most important control factor. ZnS:Mn films were then deposited on carbon, Si_3N_4, SiC and alumina substrates and their luminescence properties were investigated.

2. EXPERIMENTAL

The ZnS:Mn thin films were fabricated by rf magnetron sputtering. The sputtering system employed a normal sputtering chamber with a 7 cm-diameter target and the target-substrate distance was kept at 8 cm. The target composition was 95% ZnS and 5% Mn. Slide glasses and various ceramics (alumina, silicon nitride, silicon carbide and carbon) were used as substrates with dimensions of 2 cm × 2 cm. The substrates were ultrasonically cleaned in pure acetone, deionized water and ethanol before loading them into the growth chamber. The growth chamber was evacuated to below 2×10^{-5} Torr before high purity argon gas (99.999%) was introduced into the chamber. The crystallinity of the films was evaluated by the intensity and the full width at half maximum (FWHM) of the (111) peak of cubic ZnS (β-ZnS). Photoluminescence (PL) spectra of the films on the polycrystalline substrates were obtained with a fluorescence spectrophotometer (Hitachi F-3010). TL intensity was measured by using a photon counting system which consisted of a photon multiplier (PM) (R 464S, Hamamatsu Photonics Corp.), and a photon counter controlled by a computer (C5410-51, Hamamatsu Photonics Corp.). The test material was rotated at a speed of 150 rpm, on which a plastic rod of 2 mm in diameter at tip was applied under a load of 10 N to produce friction. The TL emission light induced by friction was guided to the PM through a glass fiber of 3 mm in diameter, and the distance between glass fiber and friction contact was set to 40 mm.

3. RESULTS AND DISCUSSION

In this study, we used L16(4^5) orthogonal array because we investigate five the sputtering factors, and their levels were four. Table 1 lists the sputtering factors and their levels. Table 2 shows the intensities and FWHM of (111) XRD peak on the 16 experiments.

TABLE 1. Factors and levels for sputtering conditions

Factors	L1	L2	L3	L4
A) Substrate temp(^{0}C)	100	150	200	250
B) rf power(W)	100	150	180	200
C) Sputt. Pressure(Pa)	0.4	0.8	1.5	3.0
D) Sputt. time(min)	30	60	90	120
E) Pre-sputt. time (min)	3	10	15	20

TABLE 2 Assignment of L16 (4^5) orthogonal arrays and results of experiments

No	Factor					Intensity (kcps)	FWHM 2(θ) (deg)
	A	B	C	D	E		
1	1	1	1	1	1	4.5	0.24
2	1	2	2	2	2	67	0.19
3	1	3	3	3	3	131	0.16
4	1	4	4	4	4	50.5	0.20
5	2	1	2	3	4	8	0.26
6	2	2	1	4	3	2.5	0.32
7	2	3	4	1	2	2	0.17
8	2	4	3	2	1	22.5	0.20
9	3	1	3	4	2	36.5	0.21
10	3	2	4	3	1	15.5	0.18
11	3	3	1	2	4	10	0.23
12	3	4	2	1	3	7	0.19
13	4	1	4	2	3	6	0.22
14	4	2	3	1	4	7.5	0.40
15	4	3	2	4	1	47.5	0.23
16	4	4	1	3	2	9.5	0.22

TABLE 3 Analysis of variance table on crystallinity of ZnS:Mn films

Factors	S	f	V	F
A) Subst. Temp.	7327.8	3	2442.1	10.2
B) Rf power	2548.6	3	849.56	3.55
C)Sputt.Pressure	4066.7	3	1355.58	5.66
D)Sputt. Time	2886.7	3	962.26	4.01
E) pre-sputt.time	718.14	3	239.38	0
ERROR(O)	718.14	3	239.38	O

Table 3 shows the ANOVA values from the crystallinity data. The symbol S represents the sum of squares; S_I is the sum of square of the i-th sputtering control factor; $S_i = \sum (X_{ij} - X)^2$, where X_{ij} are the measured values, X is the overall mean calculated from the intensity values in Table 2. X_{ij} is obtained from Table 2 .

The symbol f represents the degree of freedom of the control factors. All f values are 3 because all levels of the factors have 4 data. The symbol V represents the mean squares and is given by V = S/ f. The symbol F represents a test statistic and is given by $F = V_I / V_e$, where $V_e = S_e / f_e$. From Table 3, V_e= 239.38, f_e=3 and S_e= 718.14

Here, the pre-sputter time was taken as the experimental error because its variance is much smaller than the other factors. The F statistics of the substrate temperature, rf power, sputtering pressure, sputtering time and pre-sputtering time are; 10.20, 3.55, 5.66 and 4.01 respectively. Since the degree of freedom for all control factors is 3 and at the 5 % level, $F_{(3,3;5\%)}$ =9.28 according to the F distribution table. Since the F statistic of the substrate temperature is higher than $F_{(3,3;5\%)}$, the substrate temperature is statistically significant, whilst the F statistics of other factors are less than $F_{(3,3;5\%9}$ they are not statistically significant. Since the F statistics of the substrate temperature is the highest, the substrate temperature is the most important control factor for determining the crystallinity of the films.

Table 4 shows the effects of each level of all the factors. Here the effect means the difference between the mean of a level and X. The optimum sputtering condition is obtained if the difference is maximum because the higher the intensity the higher the degree of crystallinity of the film. From the results of Table 4, the optimum sputtering conditions are as follow: substrate temperature — 100 °C, rf power—180 W, sputtering pressure—1.5 Pa, sputtering time — 90min, pre-sputtering time — 15 min.

Since the substrate temperature was the most significant control factor for the crystallinity of the films, we investigated the effect of the substrate temperature in more detail. Keeping the other conditions constant, the substrate temperature was varied from 100 to 200 °C. From Fig. 1, a maximum peak intensity and a minimum FWHM were observed at substrate temperature of 150 °C meaning the optimum substrate temperature is 150 °C. Under the optimized sputtering conditions, ZnS:Mn films were then grown on carbon, silicon nitride, silicon carbide and alumina substrates.

TABLE 4 Effect of each level and optimum conditions

Factor	L-1	L 2	L 3	L 4	Optim
A)Subs. temp.	36.5	-17.9	-9.5	-9.0	100
B)rf power	-12.9	-3.59	20.9	-4.3	180
C)Sputt. press.	-20.0	5.66	22.6	-8.2	1.5
D)Sputt. time	-21.4	-0.34	14.2	7.5	90
E)Pre sputt. time	-4.2	2.03	9.9	-7.7	15

Table 5 Properties of ZnS:Mn films on different substrates

Subst.	carbon	SiC	Si_3N_4	α-Al_2O_3
PL (a.u.)	0.042 (10.02)	0.025 (11.56)	0.102 (43.86)	0.450 (57.58)
TL (a.u.)	19 (24)	15 (800)	47 (700)	17 (950)
FWHM (deg.)	0.172 (0.151)	0.159 (0.153)	0.158 (0.158)	0.155 (0.153)
(111) peak (deg)	28.686 (28.804)	28.622 (28.680	28.606 (28.728)	28.588 (28.720)

NB: *Figures in parentheses are values obtained after thermal annealing.*

In order to remove the internal stress caused by sputtering, post thermal annealing was carried out in an Ar/H_2 ambient at 500 °C for 1 h. Table 5 shows the PL and TL intensities, the FWHM of (111) XRD peak and the (111) peak position of the ZnS:Mn films on the polycrystalline substrates before and after annealing. From Table 5 it can be seen that, the PL and TL intensities of the films on all the substrates improved after annealing. The ZnS:Mn films after growth emitted yellow PL (excitation wavelength λ = 340 nm) peaking at about 580 nm. This improved luminescence can be explained on the basis of an improvement in crystallinity of the host (ZnS) material after annealing. This can also be seen from the decrease in the FWHM values of the (111) peak after annealing. The (111) XRD peak of the ZnS:Mn films on all the substrates shifted towards higher 2θ values after annealing. This can be attributed to the enlargement of the Mn^{2+} ions after annealing causing distortions in the host lattice. However, one major problem encountered, was the peeling of the films from the substrate during TL measurements after annealing at 500 °C. Figure 2 shows a typical TL response curves for ZnS:Mn films on glass (a) and alumina (b) after annealing at 500 °C in Ar/H_2 atmosphere. The decrease in intensity with time shows the peeling effect. This can be attributed to the large thermal mismatch between the film and substrate after annealing. Currently, we are looking for a suitable material which has similar thermal expansion coefficient with ZnS:Mn films to be used as a buffer layer to prevent peeling of the films after thermal annealing.

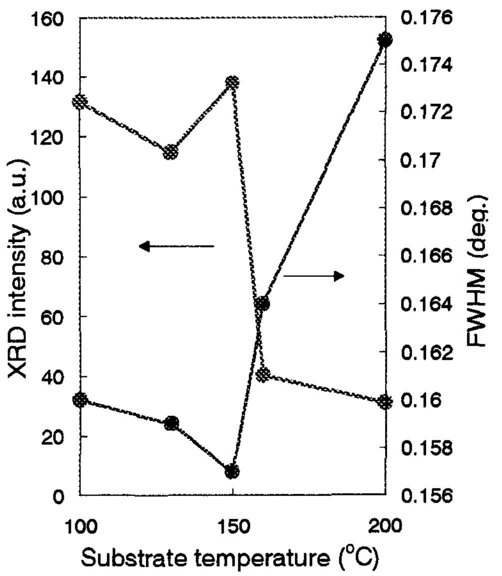

Fig.1, Dependence of crystallinity of ZnS on substrate temperature.

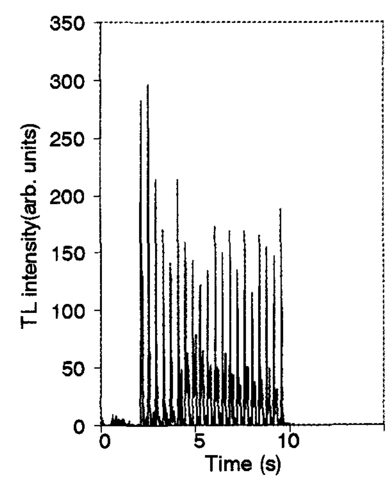

Fig.2, TL response of ZnS:Mn film on glass substrate grown at substrate temperature of 160 °C and annealed in H_2/N_2 atmosphere at 500 °C for 1hr.

4. CONCLUSION

We have successfully applied the design of experiments and ANOVA methods to optimize the sputtering conditions for preparing highly crystalline ZnS:Mn films. The substrate temperature is statistically found to be the most important sputtering factor for the crystallinity of the films. Oriented ZnS:Mn films with high crystallinity were deposited under the optimized sputtering condition on various polycrystalline substrates. After a post-annealing in Ar/H_2 atmosphere at 500 ^{0}C, high TL was obtained for these films.

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